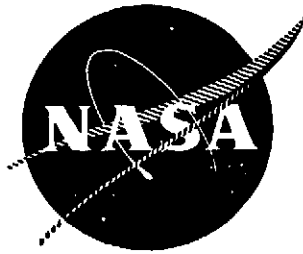


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**PROCESS DEVELOPMENT FOR
Ni-Cr-ThO₂ SHEET**

by
R. C. Cook and L. F. Norris



SHERRITT GORDON MINES LIMITED
Fort Saskatchewan, Alberta
Canada

prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA Lewis Research Center
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Ni-Cr-ThO₂ AND Ni-Cr-Al-ThO₂ SHEET
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16. Abstract <p>A process was developed for the production of thin gauge Ni-Cr-ThO₂ sheet. The process was based on the elevated temperature deposition of chromium onto a wrought Ni-2%ThO₂ sheet and subsequent high temperature diffusion heat treatments to minimize chromium concentration gradients within the sheet. The mechanical properties of the alloy were found to be critically dependent on those of the Ni-2%ThO₂ sheet. A similar process for the production of a Ni-Cr-Al-ThO₂ alloy having improved oxidation resistance was investigated but the non-reproducible deposition of aluminum from duplex Cr/Al packs precluded successful scale-up. The mechanical properties of the Ni-Cr-Al-ThO₂ alloys were generally equivalent to the best Ni-Cr-ThO₂ alloy produced in the programme.</p>					
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FOREWORD

This report was prepared by the personnel of Sherritt Gordon Mines, Fort Saskatchewan, Alberta, Canada and describes original work performed under NASA Contract NAS 3-14313.

Technical monitoring was provided by the NASA-Lewis Research Center through Project Manager, Dr. J. D. Whittenberger, of the Materials and Structures Division.

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SUMMARY

The goals of the programme were to develop a process for the production of thin gauge Ni-Cr-ThO₂ or Ni-Cr-Al-ThO₂ sheet which could meet the technical requirements of thermal protection systems on space shuttle vehicles and to provide samples of such material to NASA for evaluation in their technology application programmes. A standard process was defined which included the steps of an elevated temperature deposition of chromium from a powder pack onto a wrought Ni-2ThO₂ sheet and the homogenization of the chromium by extended heat treatment. The process was used for the production of Ni-Cr-ThO₂ sheet material in gauges of 0.25 to 0.51 mm and sizes up to 610 x 1220 mm. The mechanical properties of the resulting alloy were found to be critically dependent on those of the starting Ni-2ThO₂ sheet. The control of chromium concentration was dependent on heat treatment parameters (temperature, time, rate of heat-up, method of pack preparation).

A similar process for the production of a Ni-Cr-Al-ThO₂ alloy gave non-reproducible results due to difficulties in control of the aluminum deposition from the duplex Cr/Al pack. However, the mechanical properties of the ternary alloy produced in the programme exceeded the target values with the exception of the transverse bend ductility which exhibited a pronounced sensitivity to surface condition. In addition, the alloy possessed the greatly improved oxidation resistance inherent in the aluminum-modified system. It is believed that the difficulties in control of the aluminum composition in the alloy sheet could be eliminated through use of a nickel-rich Ni/Cr/Al pack.

A total of 12.6 kg of Ni-Cr-ThO₂ sheet in two gauges (0.25 and 0.38 mm) and 3.4 kg of Ni-Cr-Al-ThO₂ sheet at 0.25 mm thick was produced in Task IV for shipment to NASA-Lewis. Sheet sizes were up to 600 x 1200 mm.

INTRODUCTION

Dispersion strengthened metals and alloys are a new family of engineering materials which offer designers and engineers wrought metallic products that are capable of withstanding substantial stresses at temperatures near the melting point of the metal matrix. Unlike complex superalloys, these materials usually have a simple chemical composition which consists of the chosen matrix, i.e. either a pure metal or a single phase alloy, and a stable particulate dispersoid that is uniformly dispersed throughout the matrix. The strength properties of dispersion strengthened materials generally depend upon the physical characteristics of the dispersoid (size, volume fraction and distribution) and its ability to stabilize an optimum microstructure (e.g. coarse grain size or highly elongated grain shape).

This programme was initiated as part of the NASA Space Shuttle Technology Program and was designed to provide an alternative processing route for the production of thin gauge Ni-20Cr-2ThO₂ sheet material. This alloy was under consideration for use on the thermal protection system of the Space Shuttle in the temperature range 1255 to 1477 K. A manufacturing development programme was being conducted by Fansteel Inc. on the primary metallic candidate, TD NiCr (ref. 1).

The process to be studied in the current programme at Sherritt Gordon is based on the elevated temperature deposition of chromium from a powder pack onto a wrought Ni-2ThO₂ sheet (chromizing). Subsequent high temperature heat treatment effects diffusion of the chromium through the sheet thickness and thereby minimizes concentration gradients (homogenizing). This process was originally developed on a laboratory scale and is described in detail elsewhere (ref. 2). Because of a requirement for improved oxidation resistance, particularly under dynamic, low pressure conditions, a similar process was also investigated which would produce an aluminum-modified version of the Ni-Cr-ThO₂ alloy. The pack diffusion approach has been studied by Seltzer, et al (ref. 3) in attempts to provide the basic Ni-Cr-ThO₂ alloy with the required oxidation resistance but these studies were directed at introducing aluminum into the surface layers only (to a depth of about 100 µm) whereas in the current programme a uniform distribution of aluminum was desired through the strip thickness.

The objectives of the programme were as follows:

- To develop an alternative process for the production of Ni-Cr-ThO₂ or Ni-Cr-Al-ThO₂ sheet material which would meet the technical requirements of thermal protection systems on space shuttle vehicles.
- To provide material for evaluation in NASA technology programmes.

The programme was conducted in four sequential tasks as follows:

- | | |
|----------|--|
| Task I | Scale-up Feasibility Study |
| Task II | Process Development and Scale-up |
| Task III | Development of a Ni-Cr-Al-ThO ₂ Alloy |
| Task IV | Material Characterization |

RESULTS AND DISCUSSION

1. Task I Scale-up Feasibility Study

The objective of Task I was to demonstrate the feasibility of scaling up the laboratory process by conducting experiments to produce sheet sizes up to 305 x 460 mm. These studies utilized furnace facilities at General Electric's Refractory Metal Rolling Operation in Cleveland, Ohio (now AMAX Specialty Metals Corporation) and surface grinding equipment at the Hill Acme Co., also in Cleveland, Ohio.

1.1 Material Procurement

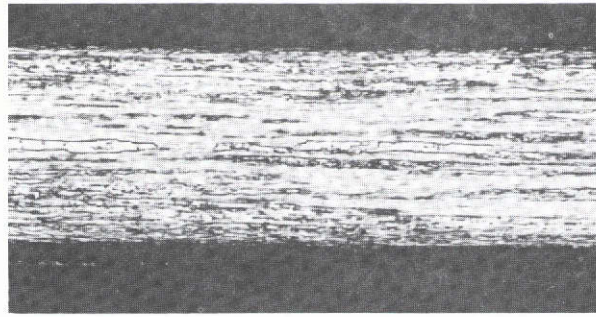
Three different lots of Ni-2ThO₂ sheet were used in Task I. Two of the lots were produced by Sherritt Gordon and had differing microstructures and gauge as shown in Figure 1. The third lot, TD Ni (heat 3120) produced by Fansteel, was included in the programme to determine the effect of sheet flatness on the results obtained in the chromizing process. The certified mechanical properties conformed to SAE specification AMD 55 DG for Ni-ThO₂ sheet products and are given in Table I. The chemical compositions of the three lots of Ni-ThO₂ are given in Table II.

TABLE I. TRANSVERSE MECHANICAL PROPERTIES FOR Ni-ThO₂ SHEET MATERIAL USED IN TASK I

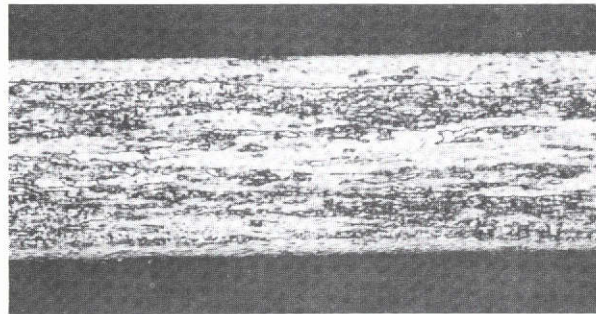
Material	Lot	Gauge mm	Room Temperature			1366 K				105° Bend Test
			0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	Stress Rupture h @ 38MN/m ²	
DS Ni	141	0.43	350	475	11	121	122	2	>20	1t
DS Ni	170	0.25	480	620	10	76	84	3	>20	1t ^a
TD Ni	3120	0.25	395	515	12	91	118	5	not certified	1t
TD Ni ^b	3120	0.25	355	465	7	95	101	3	>20	1t

a. Although certified to a 1t bend radius, many tests showed marginal pass characteristics.

b. Test results from Sherritt laboratory.

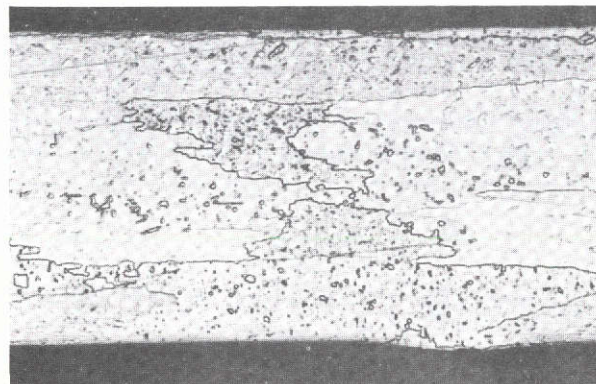


Longitudinal

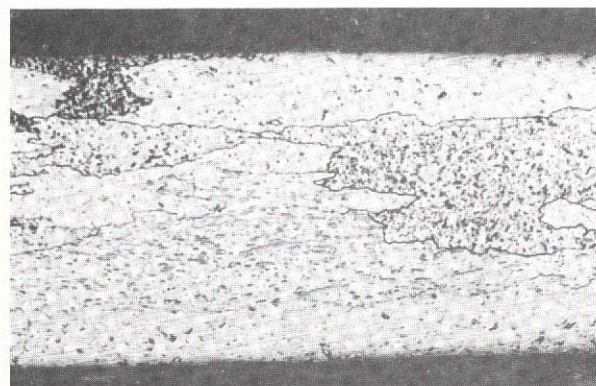


Transverse

a) DS Ni Lot 170 (x100)



Longitudinal



Transverse

b) DS Ni Lot 141 (x100)

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FIGURE 1. MICROSTRUCTURES OF DS Ni SHEETS USED IN TASK I STUDIES
ETCHANT - 10% SOLUTION OF 50/50 KCN AND $(\text{NH}_4)_2\text{S}_2\text{O}_8$

TABLE II. CHEMICAL COMPOSITION OF Ni-ThO₂ SHEET MATERIAL USED IN TASK I

Composition in Weight Percentage								
Sheet	Co ^a	Cu ^a	Fe	S	C	Cr ^a	ThO ₂	Ni
DS 141	0.001	0.001	0.025	0.001	0.003	0.001	2.2	bal.
DS 170	0.001	0.002	0.02	0.001	0.009	0.001	2.3	bal.
TD N1	0.06	0.006	0.007	0.001	0.0053	0.002	2.55	bal.

a. Emission spectrograph estimates.

A chromizing pack consisting of Cr/4Y₂O₃ powder (-325 mesh) was selected for the initial trial rather than the proposed composition of Cr/50Al₂O₃ in order to compensate for the lower-than-anticipated maximum furnace temperature of 1500 K. In addition to having a low sintering rate the Cr/Y₂O₃ pack provided increased chromium deposition at any given temperature due to the much increased contact area between the Ni-ThO₂ sheet and the chromium powder. The chromizing retort was a simple, open-topped, mild steel box measuring 80 x 360 x 610 mm with a 12 mm thick steel lid.

1.2 Preliminary Process Definition

The chromizing procedure consisted of partially filling the retort with the Cr/Y₂O₃ powder, placing a Ni-ThO₂ sheet on the levelled pack and then covering the sheet with additional chromizing powder. A modest amount of vibration settled the pack and the charge (about 50 kg) was placed into the chromizing furnace in a dry hydrogen atmosphere at 1500 K. Chromizing time per furnace cycle was variable and in the range 6 to 20 h in order to determine deposition as a function of time. The amount of chromium deposition was determined by weight gain measurements following each cycle and for comparative purposes was reported as weight gain per unit area of sheet. Chromium concentrations were also calculated as percentages and are reported as equivalent % Cr.

The temperature profile and heat-up curve for a representative chromizing cycle were determined and the results are shown in Figures 2 and 3. Steady state operation was achieved during the cycle in approximately 1.5 h at which time the temperature at the center of the sample sheet varied by ± 1 K.

Four sheets of 305 x 460 mm Ni-ThO₂ were chromized at 1500 K in an attempt to define a preliminary working process and to isolate any problem areas. The resulting chromizing data are shown in Table III.

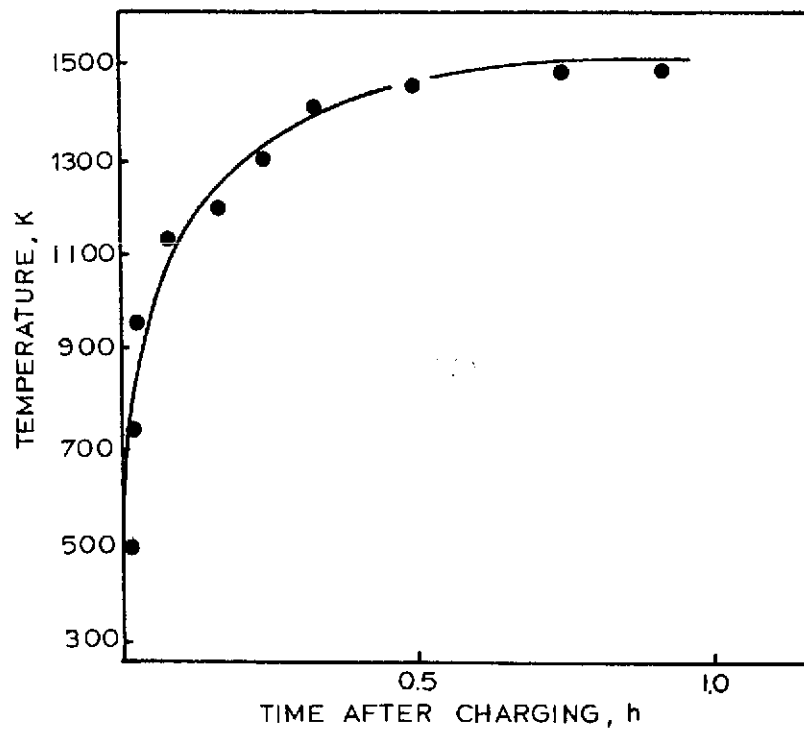


FIGURE 2. HEAT-UP RATE FOR CHROMIZING PACK CHARGED TO FURNACE AT 1500 K

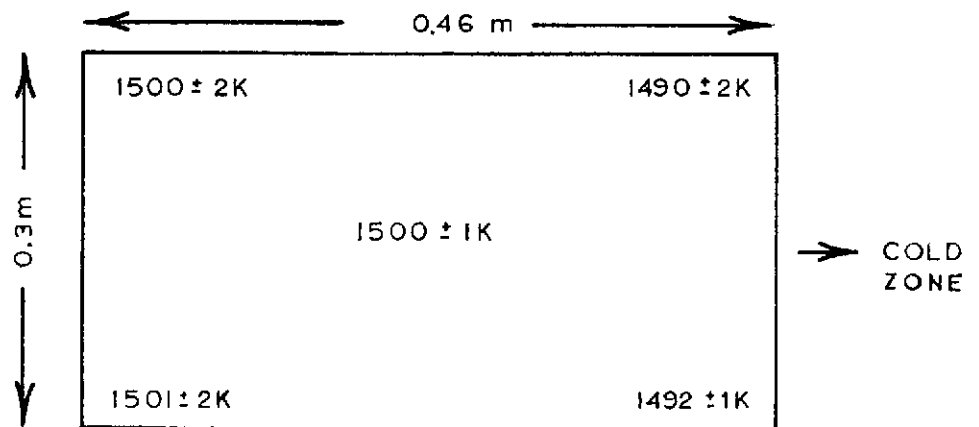


FIGURE 3. STEADY STATE TEMPERATURE CONFIGURATION (2 h AFTER CHARGING)

TABLE III. SUMMARY OF CHROMIZING DATA FOR SHEETS 1 THROUGH 4

Sheet/Lot	1/141	2/141	3/170	4/141
Ni-ThO ₂ Gauge (mm)	0.43	0.43	0.25	0.43
Time at 1500 K (h)	51	51	23	58
Number of Furnace Cycles	3	3	2	4
Chromium Deposition (kg/m ²)	0.47	0.48	0.31	0.50
Equivalent % Cr	19.7	19.7	20.7	20.1

Sheets 1 and 2 were designed to show the reproducibility of chromium deposition and Sheet 4, with four furnace cycles, was processed to obtain weight gain values at intermediate chromizing times. Sheet 3 was included to obtain general processing data on thinner gauge Lot 170 material.

Sheet 1 was sampled for duplicate wet chemical analyses to determine the uniformity of chromium deposition at various positions in the sheet. These analytical results are presented schematically in Figure 4.

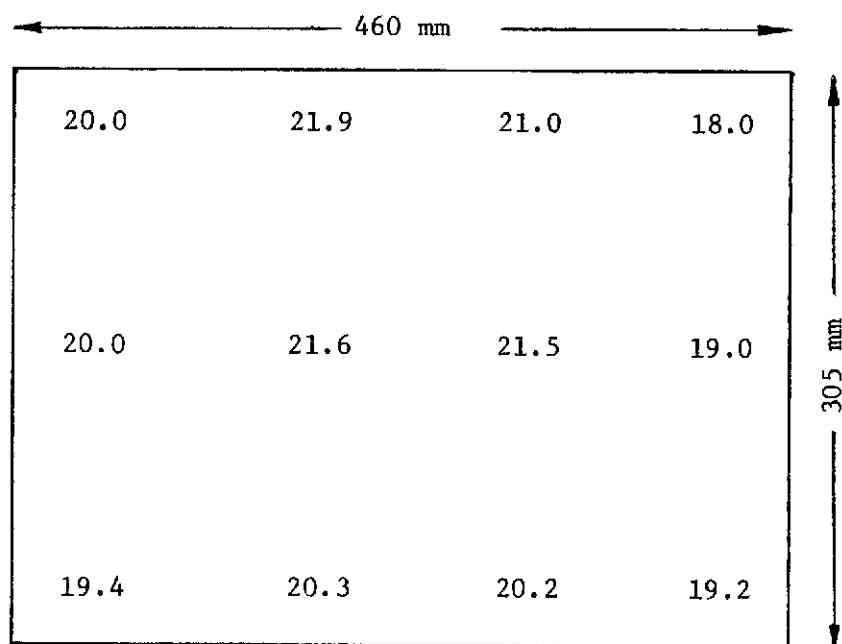


FIGURE 4. CHROMIUM CONCENTRATION (IN WEIGHT PERCENT) AT VARIOUS POSITIONS IN SHEET 1 AFTER CHROMIZING FOR 51 h AT 1500 K

Samples from Sheets 1, 2 and 3 were annealed at 1500 K for various times up to 100 h to determine the minimum time required to reduce the chromium gradient through the thickness of the sheet to approximately 1% (i.e. 20% Cr on the surface, 19% Cr in the center). Electron microprobe analysis of these samples showed that a 1% chromium gradient could be achieved using a 30 h anneal at 1500 K for the 0.25 mm sheet (Sheet 3) and 48 h for the 0.43 mm sheets (Sheets 1 and 2). Figure 5 shows schematic microprobe results for the homogenization of the chromium gradients in the latter two sheets.

Wide belt abrasive grinding experiments, to remove the surface porosity that developed during homogenizing, were done at the Hill Acme Company in Cleveland, Ohio, using partially homogenized Sheets 2 and 3. The general objective of these trial tests was to determine the grinding conditions necessary to produce an acceptable surface finish and gauge tolerance. Sheet 2 was ground to 0.48 mm from 0.58 mm and Sheet 3 to 0.25 mm from 0.33 mm. The use of wet grinding with 80 to 120 grit SiC belts was found to give satisfactory surface finish and permit a good rate of stock removal. Sheet 3 was sheared into small pieces for a check on the thickness control at the low gauge. With the exception of small thinned areas near the sheet ends and edges approximately 90% of the thickness measurements were within the range 0.244 to 0.263 mm.

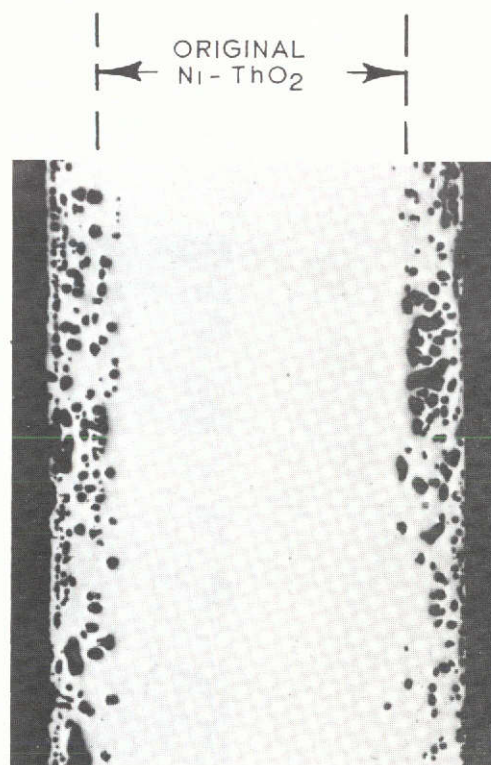
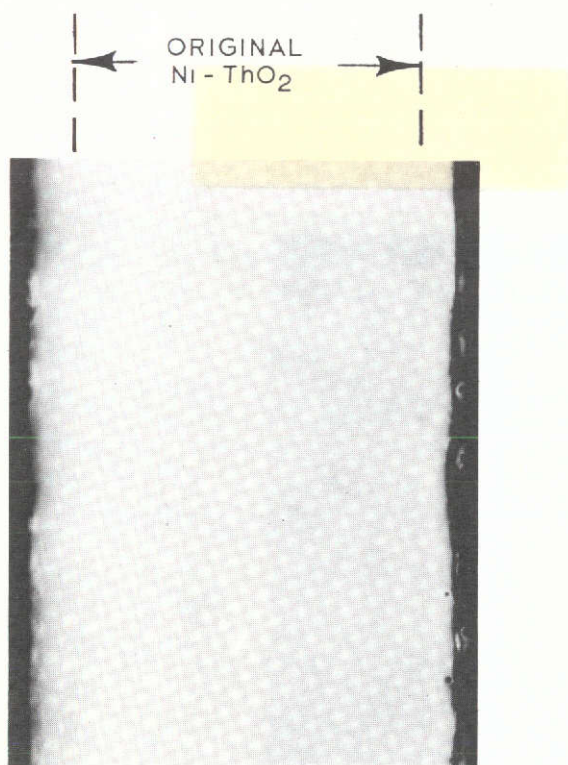
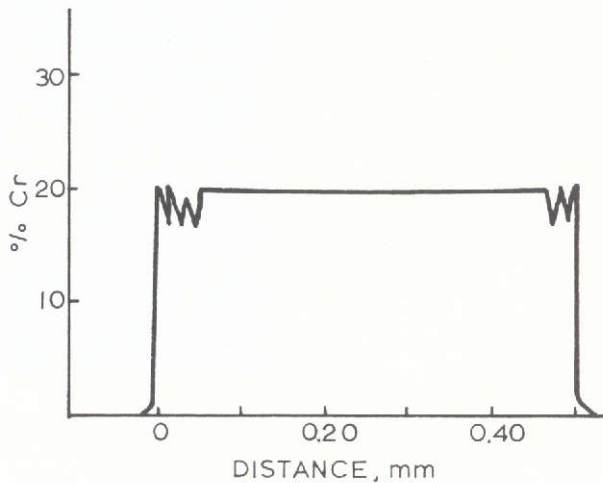
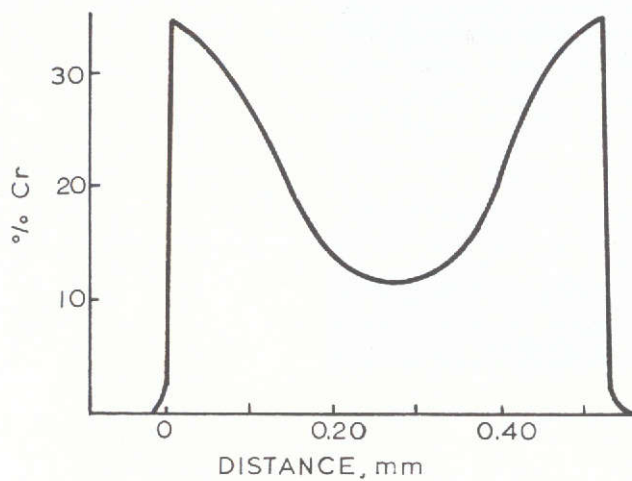
Several areas of technical difficulty were defined in the preliminary process definition studies and these are itemized and discussed below:

(i) Material Procurement

- The microstructure of the thin gauge (Sheet 3) chromized and homogenized samples was generally uniform but the microstructure of the thicker chromized and homogenized samples (Sheets 1, 2 and 4) exhibited some internal porosity and massive thoria-free regions associated with grain boundaries (Figure 6). This phenomenon had been observed previously and Whittenberger (ref. 4) has proposed that the thoria-free regions are due to grain boundaries acting as vacancy sources. Thoria-free areas were expected in Sheet 3 but are not clearly visible in Figure 6a. It was concluded that a coarse grain Ni-ThO₂ structure was not desirable for chromizing.
- The level of selected contaminant elements in the sheets (iron, sulphur) increased during chromizing. The increase in iron concentration (0.02 to 0.07%) was attributed to a high iron content of the Cr/Y₂O₃ powder and also to contamination of the Cr/Y₂O₃ powder by the mild steel retort. The level of sulphur increased from 0.001% to 0.01% and was also attributed to the Cr/Y₂O₃ powder.

(ii) Chromizing

- Procedures would be required to ensure 100% contact between the chromizing pack and both sides of the Ni-ThO₂ sheet. The obvious result of having less than this degree of contact was areas of low chromium concentration. Powder contact with the top surface

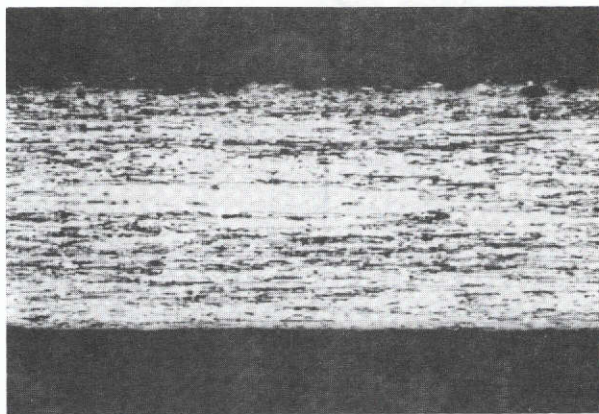


a) After chromizing for 51 h at 1500 K, unetched

b) After chromizing for 51 h at 1500 K and homogenizing for 48 h at 1500 K, unetched

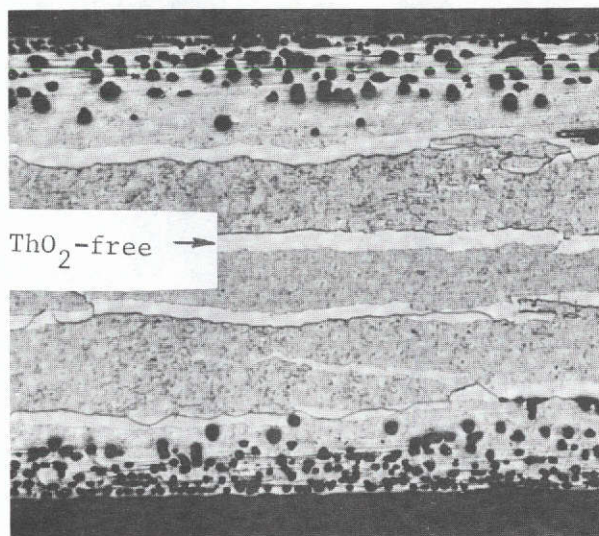
FIGURE 5. SCHEMATIC ELECTRON MICROPROBE RESULTS OF IN-PROCESS SHEETS FROM DS Ni LOT 141 (x100)

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a) Sheet 3 (Lot 170 DS Ni)

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b) Sheet 1 (Lot 141 DS Ni)

FIGURE 6. MICROSTRUCTURES OF UNGROUND Ni-Cr-ThO₂ SHEETS PRODUCED FROM DS Ni WITH DIFFERENT MICROSTRUCTURES (x100)
ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

of the sheet was not difficult to maintain but if shrinkage of the pack occurred or if the retort sagged and allowed powder movement, cavities developed below the bottom surface of the sheet thereby reducing chromium deposition in those areas. The flatness of the Ni-ThO₂ sheet was also important in that the chromizing pack did not easily conform to the contours of a wavy, buckled sheet.

(iii) Surface Grinding

- Edge thinning and non-uniform stock removal during grinding produced gauge variations within the final product. A flatter Ni-Cr-ThO₂ product after chromizing and homogenizing would result in more uniform stock removal and a combination of a firmer contact roll and a wider carrier plate would reduce edge thinning during surface grinding.

1.3 Process Demonstration

Eight sheets of 0.25/0.28 mm Ni-ThO₂ sheet were pack chromized to nominally 20% Cr, homogenized for 40 h at 1500 K and surface finished to produce 0.28 mm thick x 305 x 460 mm Ni-Cr-ThO₂ sheet to demonstrate the feasibility of the process. Selected changes were made in the process in attempts to solve problems encountered during the preliminary studies. These process changes were as follows:

- (i) A Ni-ThO₂ sheet with a fine grained elongated microstructure was used for chromizing (Lot 170). No recurrence of internal porosity or massive thoria-free regions was observed.
- (ii) A Cr/Y₂O₃ powder containing less iron was successfully used to reduce iron contamination.
- (iii) A retort designed for vertical loading was used during the chromizing of two sheets (5 and 6) in an attempt to eliminate cavities between the pack and the sheet. However, sagging of the retort resulted in powder movement and non-uniform chromium deposition.
- (iv) An increased number of furnace cycles (from 2 to 3) gave a much improved chromium distribution over the surface of the sheets.
- (v) The length of the first furnace cycle was reduced so as to give a balanced chromium deposition (e.g. 14% Cr on the first increasing to 20% on the second cycle rather than 18% increasing to 20% as was the case for Sheet 3 in the preliminary studies).
- (vi) Two Ni-ThO₂ sheets (TD Ni Heat 3120; Sheets 11 and 12) with superior flatness were processed to Ni-Cr-ThO₂ and they clearly demonstrated that the flatness of the product sheet was a direct function of the flatness of the initial Ni-ThO₂ sheet.

- (vii) All sheets were surface finished using a wider carrier plate and a firmer contact roll to reduce edge thinning. The surface finish varied from an estimated 560 to 350 nm RMS as grinding progressed and gauge control near the edges was generally ± 0.013 mm.

The chromizing data are summarized in Table IV and Figure 7 shows the reproducibility of chromium deposition for all sheets, including those processed during the preliminary studies.

TABLE IV. SUMMARY OF CHROMIZING DATA FOR SHEETS 5 THROUGH 12

Sheet/Lot	5/170	6/170	7/170	8/170	9/170	10/170	11/ TD Ni	12/ TD Ni
Ni-ThO ₂ Gauge (mm)	0.25	0.28	0.28	0.28	0.28	0.28	0.27	0.27
Time at 1500 K (h)	29	29	27	26	28	28	27	27
Number of Furnace Cycles	3	3	2	2	2	2	2	2
Chromium Deposition (kg/m ²)	0.32	0.33	0.33	0.33	0.33	0.32	0.30	0.31
Equivalent % Cr	21.3	20.5	20.3	20.5	20.2	19.7	20.7	20.7

1.4 Evaluation of Process Demonstration

1.4.1 Chromium Concentration and Gauge Uniformity

Sheets 6, 8 and 11 were sheared initially into 102 x 102 mm pieces from which samples for tensile testing were sheared. Edge clippings from the tensile samples provided material for bend testing, metallography and electron microprobe analysis. A typical microstructure is shown in Figure 8.

The remaining area was sheared into 25 x 40 mm samples for thickness measurements and x-ray fluorescence determination of the surface chromium distribution. Wet chemical analyses were done on selected samples following the fluorescence analysis.

Chromium concentration contour maps for both sides of Sheet 8 are shown in Figure 9. The maps were generated using approximately 160 duplicate x-ray fluorescence determinations. A frequency plot and calculated statistical information for these values are shown in Figure 10. Since the longitudinal edges accounted for most of the low chromium concentrations, a 25 mm strip was sheared from these edges, making the overall product 254 x 460 mm.

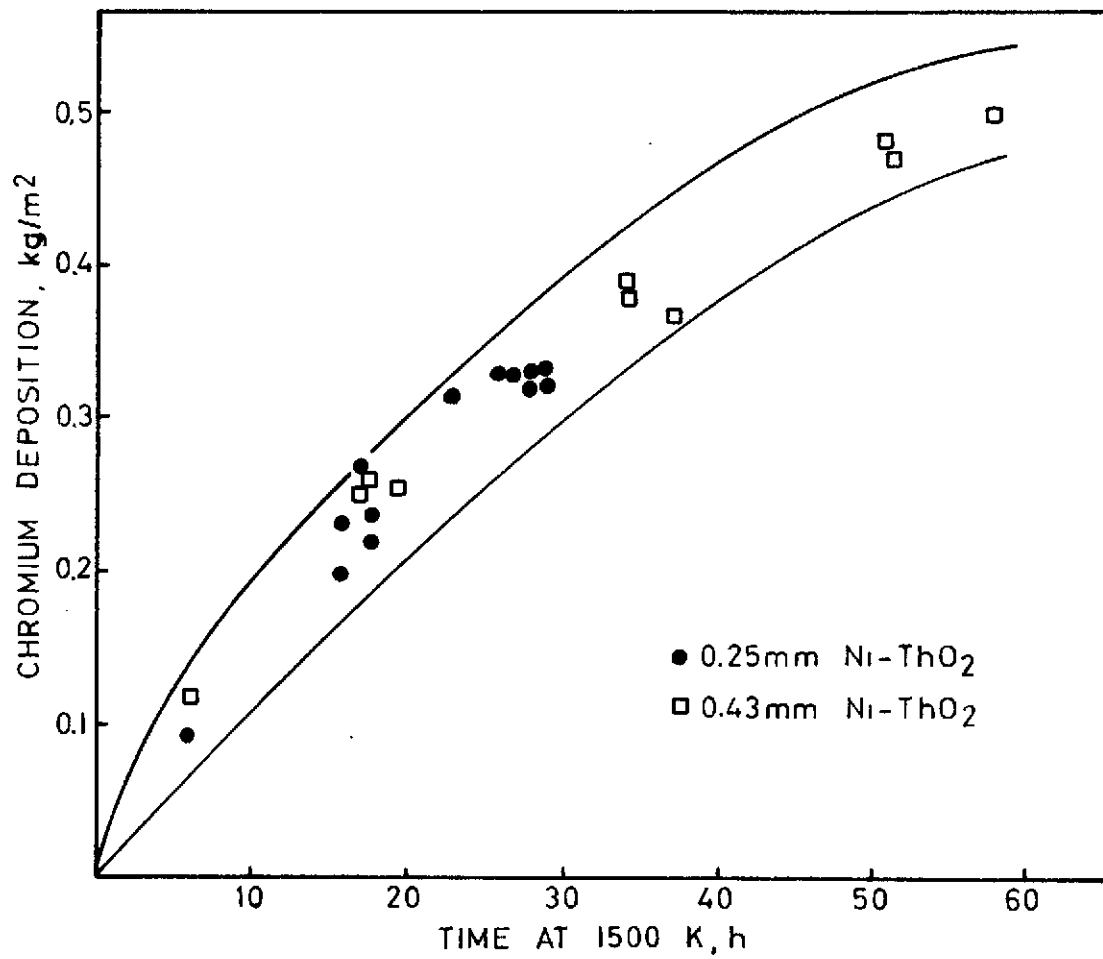


FIGURE 7. EFFECT OF CHROMIZING TIME ON CHROMIUM DEPOSITION ON Ni-ThO₂ SHEET



FIGURE 8. TRANSVERSE MICROSTRUCTURE OF Ni-Cr-ThO₂ SHEET 8 (x200)
ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

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A contour map of gauge variations in Sheet 8 was prepared from approximately 100 thickness measurements and is shown in Figure 11. Removal of 25 mm from the longitudinal edges eliminated all thickness measurements below 0.28 mm. The 95% confidence range for the sheared product was 0.298 ± 0.015 mm.

These analyses together with the selected check analyses of samples from other sheets in the demonstration trial led to the following general observations for all Task I material:

1. Wet chemical analyses and electron microprobe studies confirmed the nature of the chromium distribution as depicted by the contour maps. Both techniques showed chromium contents as low as 15 to 16% in areas which were within the 17 to 18% Cr contours near the sheet edges. Electron microprobe traces through the sheet thickness showed various chromium profiles including:
 - (a) No chromium gradient.
 - (b) A constant chromium gradient from one side to the other, and
 - (c) Surface-to-center gradients.

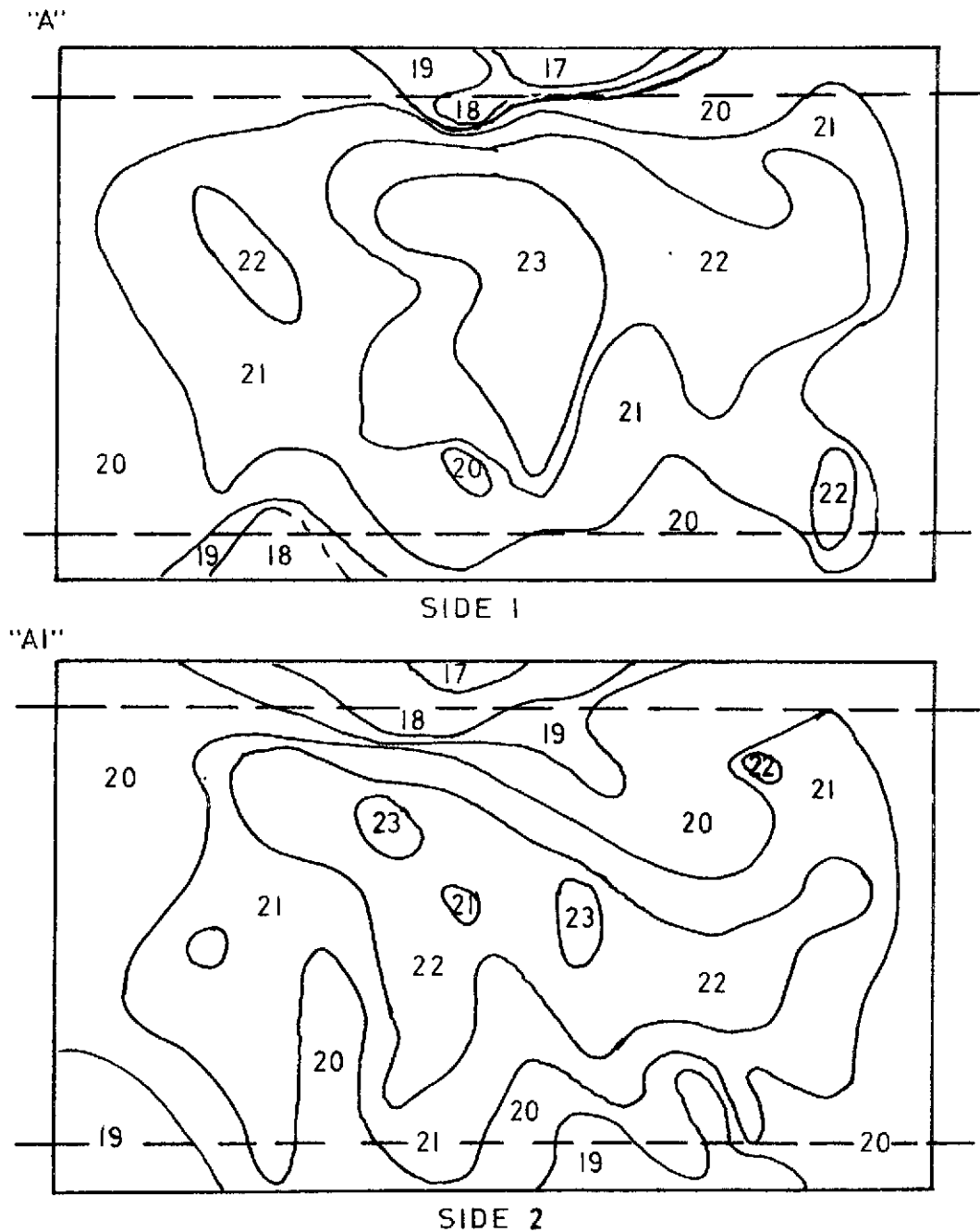
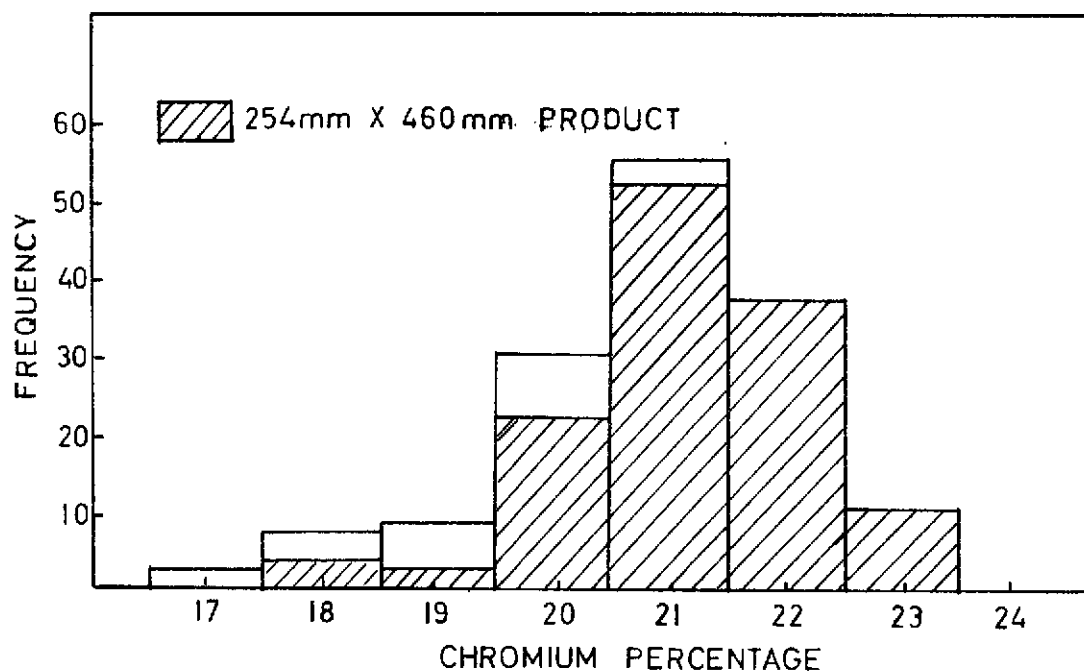


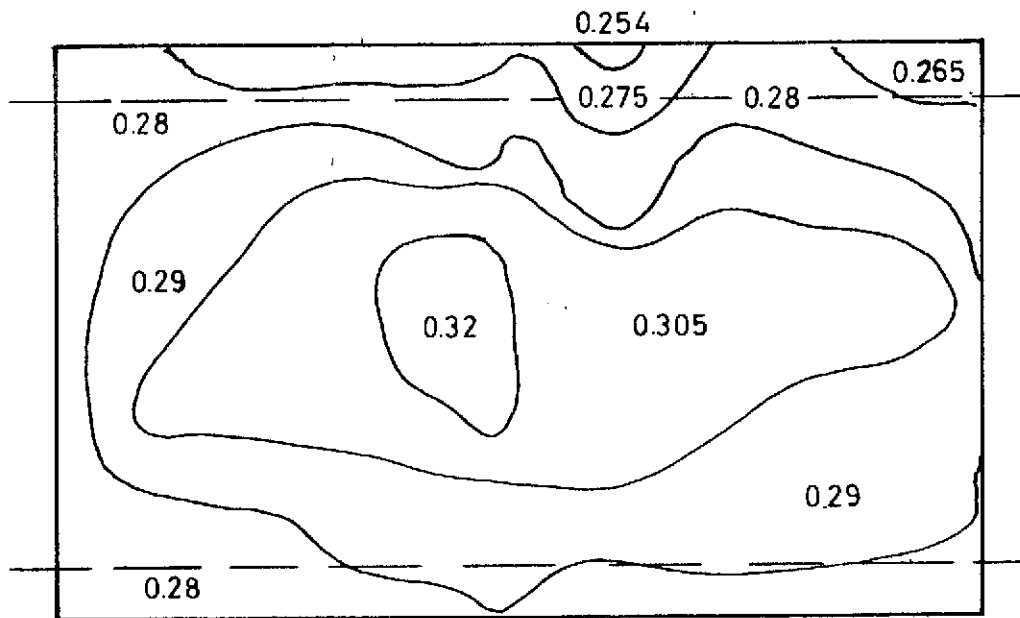
FIGURE 9. CHROMIUM CONCENTRATION CONTOUR MAPS AS DETERMINED BY X-RAY FLUORESCENCE FOR Ni-Cr-ThO₂ SHEET 8 SHEET SIZE IS 305 x 460 mm. LONGITUDINAL DOTTED LINES INDICATE 254 x 460 mm PRODUCT. "A" AND "A1" ARE COMMON.



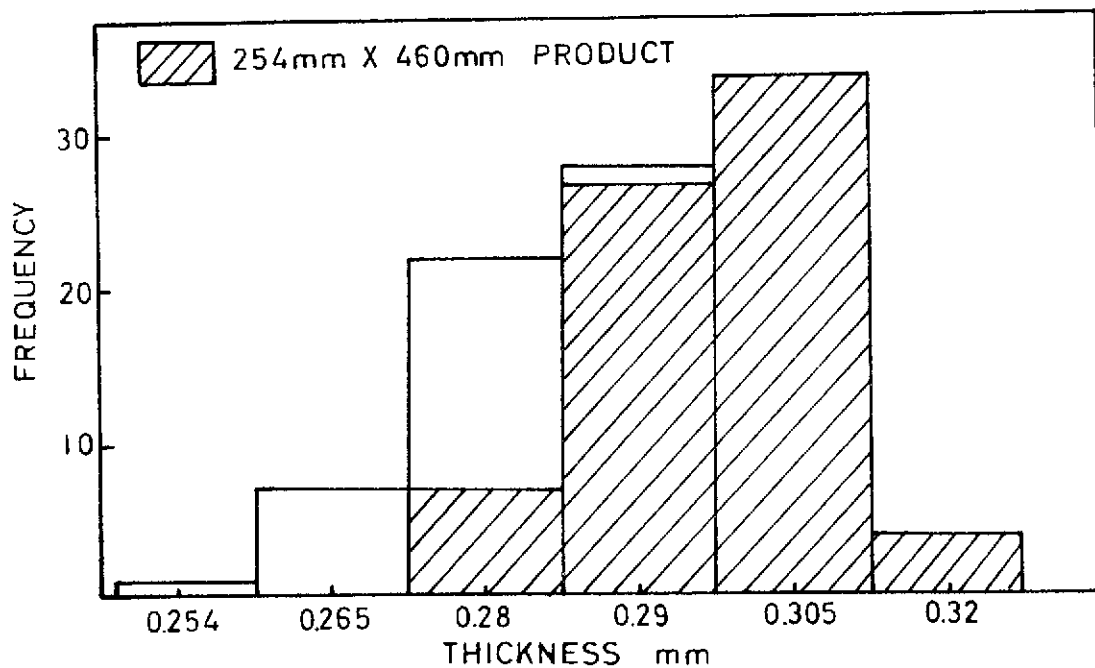
Statistical Data

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Sample Size	157	132
Mean	20.8%	21.2%
Mode	21	21
Median	21	21
Standard Deviation	1.3%	1.2%
95% Confidence Range	20.8 ± 2.1%	21.2 ± 2.0%

FIGURE 10. STATISTICAL PRESENTATION OF VARIATIONS IN CHROMIUM CONTENT IN SHEET 8



(a) Thickness Contour Map



(b) Statistical Presentation of Variation in Thickness (to closest 0.005 mm)

FIGURE 11. THICKNESS VARIATIONS (mm) IN GROUND Ni-Cr-ThO₂ SHEET 8
SHEET SIZE IS 305 x 460 mm. LONGITUDINAL DOTTED LINES
INDICATE 254 x 460 mm PRODUCT.

Maximum variations observed were 18% Cr on one side to 22% Cr on the other side (b) and 20% Cr on each surface decreasing to 18% Cr at the center (c). Surface-to-center gradients would have been reduced by increasing the length of the homogenization anneal but surface-to-surface gradients were a function of the nature of the chromium deposition and were therefore controlled by retort design and chromizing parameters; such surface-to-surface gradients could only be reduced by prolonged homogenization anneals.

2. The longitudinal edges of the sheets accounted for the majority of the low chromium analyses (less than 19% Cr). These same areas accounted for the lower gauge measurements (less than 0.28 mm).
3. Two methods appeared feasible for decreasing the variations in chromium content and in gauge in the final sheets. The first, and simplest, was to shear undesirable material from the sheet. The effectiveness of this technique had been shown previously in Figures 9, 10 and 11. Approximately 60% of the values below 19% Cr were eliminated as were 100% of the gauge values below 0.28 mm. The second method was to reinforce the retort sides to reduce sagging and increase the retort width to provide at least 75 to 100 mm clearance between the Ni-ThO₂ sheet and the retort sides. These modifications were expected to improve the contact between the chromizing pack and the edges of the Ni-ThO₂ sheet. The increase in chromium deposition rate would avoid the necessity of having to include extensive edge shearing in the processing.
4. The tendency towards the formation of a single area high in chromium at the sheet center was less pronounced for sheets processed from flatter Ni-ThO₂ sheet and for sheets chromized in three rather than two furnace cycles.

1.4.2 Mechanical Properties

Evaluation of the mechanical properties and chemical composition of sheets representative of those produced during Task I gave the results in Table V. Table VI shows results achieved with TD Ni starting material. Compared with the starting Ni-ThO₂ sheet (see Tables I and II) the Ni-Cr-ThO₂ sheets had:

- increased yield strength, ultimate tensile strength and ductility at room temperature.
- slightly increased yield strength and ultimate tensile strength at 1366 K.
- equivalent stress rupture life and elongation at fracture at 1366 K.
- equivalent bend and cup ductility; the high incidence of transverse bend failures shown in Table V was typical of the Ni-ThO₂.
- increased levels of iron and sulphur.

The above comparison suggests that the properties of the Ni-Cr-ThO₂ alloy are a function of those of the parent Ni-ThO₂ alloy and further that it may be possible to produce tailored Ni-Cr-ThO₂ alloys through control of the properties of the Ni-ThO₂ alloy.

TABLE V. REPRESENTATIVE MECHANICAL PROPERTIES AND CHEMICAL COMPOSITION OF Ni-Cr-ThO₂ SHEETS PRODUCED DURING TASK I USING DS Ni LOT 170 (SHEETS 5 THROUGH 10)

Mechanical Properties ^a	Longitudinal	Transverse							
<u>Room Temperature</u>									
0.2% Yield Strength, MN/m ²	720	690							
Ultimate Tensile Strength, MN/m ²	920	850							
% Elongation ^b	9.5	12.5							
<u>1366 K</u>									
0.2% Yield Strength, MN/m ²	113	81							
Ultimate Tensile Strength, MN/m ²	135	92							
% Elongation ^b	5	3							
Stress Rupture, 100 h life, MN/m ²	68	37							
% Elongation at Fracture ^b	3	4							
<u>Bend Test</u> , 105° around 2t radius	pass	30% pass							
<u>Cup Tests</u> , height at fracture, mm	5.6								
Chemical Composition (weight percentage)									
<u>Ni</u>	<u>Cr</u> ^c	<u>Co</u> ^d	<u>Cu</u> ^d	<u>Fe</u>	<u>Mn</u>	<u>S</u>	<u>C</u>	<u>ThO₂</u>	<u>Excess O₂</u>
bal.	18-22	0.002	0.006	0.07	0.1	0.008	0.006	1.9	<0.01

a. Average of data for Sheets 6 and 8.

b. Elongations measured in a 25.4 mm gauge length.

c. See text.

d. Emission spectrographic estimate.

TABLE VI. REPRESENTATIVE MECHANICAL PROPERTIES OF Ni-Cr-ThO₂ SHEETS
PRODUCED DURING TASK I USING TD-Ni HEAT 3120 (SHEETS 11 AND 12)

Mechanical Properties	Longitudinal	Transverse
<u>Room Temperature</u>		
0.2% Yield Strength, MN/m ²	575	690
Ultimate Tensile Strength, MN/m ²	820	755
% Elongation ^a	11	17
<u>1366 K</u>		
0.2% Yield Strength, MN/m ²	98	96
Ultimate Tensile Strength, MN/m ²	113	109
% Elongation ^a	3	3
Stress Rupture, 100 h life, MN/m ²	54	52
% Elongation at Fracture ^a	1	1
<u>Bend Test</u> , 105° around 2t radius	pass	pass

a. Elongations measured in a 25.4 mm gauge length.

The effect of secondary cold work on the mechanical properties of as-processed Ni-Cr-ThO₂ sheet (chromized, homogenized and surface ground) was also studied. Samples of Sheets 5 and 11 were cold rolled 10 to 40% and annealed for 0.5 h at 1366 to 1589 K. The mechanical properties of Ni-Cr-ThO₂ Sheet 5 after 15 and 30% cold rolling and a 1477 K anneal are compared with those of the as-processed sheet in Table VII.

All of the samples that were cold worked less than 30% and then annealed retained the fibrous microstructure of the as-processed Ni-Cr-ThO₂ product (Figure 12a). These samples had improved bend ductility at room temperature but the strength at 1366 K was reduced and remained anisotropic. Annealing the samples which were rolled 30% or more resulted in recrystallization of the microstructure to equiaxed grains approximately 10 μ m in diameter (Figure 12b). These samples showed improvement in both bend and tensile ductility at room temperature. The high temperature strengths were lower than in the as-processed condition but were isotropic and at a level not much below that of the as-processed transverse samples.

TABLE VII. EFFECT OF SECONDARY COLD WORK ON MECHANICAL PROPERTIES OF SHEET 5

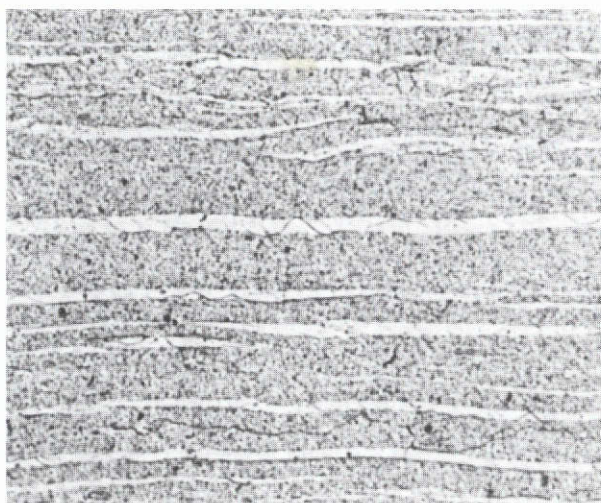
Mechanical Properties		As-Processed	Cold Rolled 15% + Anneal	Cold Rolled 30% + Anneal
<u>Room Temperature</u>				
0.2% YS, MN/m	L	720	770	630
	T	690	700	690
UTS, MN/m	L	920	950	870
	T	850	850	850
% Elongation ^a	L	9.5	11	15
	T	12.5	11	12
<u>1366 K</u>				
0.2% YS, MN/m	L	113	95	61
	T	81	55	66
UTS, MN/m	L	135	117	84
	T	92	71	79
% Elongation ^a	L	5	4	4
	T	3	4	3
Bend Test, 105° around 2t radius	L	passed	passed	passed
	T	30% passed	passed	passed

a. Elongations measured in a 25.4 mm gauge length.

1.5 Task Completion

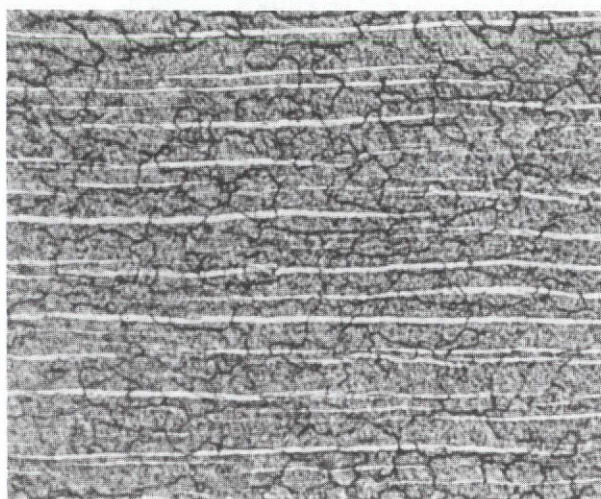
The results of the studies in Task I indicated the feasibility of scaling up the pack chromizing process to produce sheets 610 x 1220 mm. The recommendation that the programme continue into Task II (Process Development and Scale-up) was approved by the NASA Project Manager.

Three sheets (7, 9 and 10) with dimensions 0.28 x 305 x 460 mm and weighing 1 kg were shipped to NASA-Lewis to satisfy the Task I material requirements.



a) Cold Rolled Less than 30% and Annealed

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b) Cold Rolled Greater than 30% and Annealed

FIGURE 12. MICROSTRUCTURES OF COLD ROLLED AND ANNEALED SAMPLES OF Ni-Cr-ThO₂ SHEET 5 (x500)
ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

2. Task II Process Development and Scale-Up

The scale-up to larger sheet at Sherritt Gordon necessitated the procurement of a large furnace suitable for operation in the temperature range required for the chromizing process and with a low dew point hydrogen atmosphere. A grant from the Defence Research Board of the Canadian Government (Grant No. 7510-66) allowed the design and purchase of the higher temperature box furnace and hydrogen purification system detailed in Appendix A. This system was constructed by Canefco Ltd., Scarborough, Ontario, and was installed in the Rolling Mill complex at Sherritt Gordon's Fort Saskatchewan operation.

2.1 Material Procurement

Laboratory studies had demonstrated that less sintering of the chromizing pack would occur if ThO_2 was substituted for Y_2O_3 . As a result of this, a chromizing pack consisting of $\text{Cr}/5\text{ThO}_2$ (nominally -325 mesh) was prepared for use in the Task II Process Development Studies.

The Ni-ThO_2 sheet stock was procured from four distinct production lots so that data could be produced to demonstrate if the sheet chromizing approach to alloy production was independent of changes which could be expected in the characteristics of the Ni-ThO_2 sheet. It was originally intended that all sheet stock necessary to complete the programme should be purchased during Task II but the inclusion of work on a Ni-Cr-Al-ThO_2 alloy ultimately imposed restrictions on the type of Ni-ThO_2 sheet stock required for optimum properties. As a result some of the material required for Tasks III and IV was purchased after the completion of Task II. The distribution of sheets by thickness and production lot is summarized in Table VIII. Lots 1 through 3 were DS Ni produced by Sherritt Gordon and Lot 2A was TD Ni produced by Fansteel (Heat 3293). All sheets were nominally 635 x 1270 mm in size. The certified mechanical properties and chemical composition of the sheet material are presented in Tables IX and X.

TABLE VIII. Ni-ThO_2 SHEET LOT SHIPMENTS

Gauge	Number of Sheets			
mm	Lot #1	Lot #2	Lot #2A (TD Ni Heat 3293)	Lot #3
0.25	0	4	0	7
0.38	20	14	2	14
0.51	0	4	0	4

TABLE IX. TRANSVERSE MECHANICAL PROPERTIES OF Ni-ThO₂ SHEET

Lot	Room Temperature					1366 K			
	Gauge mm	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	105° Bend Test	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	Stress Rupture h @ 38MN/m ²
1	0.38	310	475	12	1t	77	88	2	>20
2	0.25	450	580	7	1t	66	97	4	10
	0.38	460	570	8	1t	79	104	3	>20
	0.51	440	570	11	1t	81	95	4	18
3	0.25	455	585	8	1t	61	72	3	10
	0.38	435	555	12	1t	89	97	3	>20
	0.51	425	565	13	1t	80	90	3	18
2A	0.38	380	495	12	4t	120	124	3	>20
2A ^a	0.38	355	460	10	1t	81	116	2	>20

a. Tested at Sherritt Gordon.

TABLE X. CHEMICAL COMPOSITION OF Ni-ThO₂ SHEET

Lot	Composition in Weight Percentage							
	Ni	Co	Cu	Fe	Cr	S	C	ThO ₂
1	bal.	<0.001	<0.001	0.02	<0.001	0.001	0.002	2.1
2	bal.	<0.001	<0.001	0.02	<0.001	0.001	0.002	2.0
3	bal.	0.001	0.002	0.02	0.001	0.001	0.002	2.1
2A	bal.	0.03	0.002	0.004	0.002	0.0015	0.001	2.0

Evaluation of samples from Lot #1 showed that the mechanical properties and chemical composition were within SAE specification AMD 55 DG. The microstructure, however, was characterized by coarse grains and therefore was unsuitable for processing to final product because of the extensive internal porosity known to develop during the homogenization anneal. Sheets from this lot were used in determining parameters only in the chromium deposition phase of the programme.

Material in Lots 2 and 3 generally met AMD 55 DG specifications but stress rupture life and room temperature ductilities were slightly below specification levels.

The certified elevated temperature strength of the TD Ni sheets (Lot 2A) was generally superior to that of the DS Ni sheets. Testing at Sherritt, however, gave tensile strengths comparable to those of the best DS Ni.

Two of the 0.38 mm thick sheets from Lot 2 were obtained in an un-annealed (as-cold rolled) condition so that a chromizing experiment could be conducted on dead flat fine grain material. The improved flatness was expected to facilitate more intimate contact between the sheet and the chromizing pack.

2.2 Laboratory Support Experiments

Two areas of interest in the Process Variable Studies to be conducted in Task II were investigated on a laboratory scale. The effects of chromium powder size and of surface condition of the Ni-ThO₂ sheet on the chromium deposition rate should be independent of sheet size and could therefore be studied more conveniently in laboratory experiments.

The chromizing pack material used in Task I was screened to provide +150 and -400 mesh fractions. Samples of 0.28 mm Ni-ThO₂ were pack chromized for 19 h at 1477 K in each of the two size fractions with the following results:

<u>Cr Size (Mesh)</u>	<u>Cr Deposition (kg/m²)</u>
+150	0.14
-400	0.17

The measured difference was marginally significant but supported the model that a finer powder provides better contact with the surface of the Ni-ThO₂ sheet. One disadvantage associated with using the +150 mesh fraction was the much lower powder apparent density (2.0 g/cm³ as compared with 2.8 g/cm³ for the -400 mesh fraction) which led to increased pack separation from the Ni-ThO₂ sheet. In all coarse powder experiments extensive pack shrinkage resulted in non-uniform chromium deposition. An optimum powder size may exist when trade-offs between deposition rate and ease of handling or uniformity of chromium deposition are considered but the difference shown in these experiments did not justify further work.

The effect of Ni-ThO₂ sheet surface condition was investigated using chromizing conditions of 22 h at 1477 K. The results summarized below suggested that the process was relatively insensitive to sheet preparation prior to chromizing and no further work was done in this area.

<u>Surface Condition</u>	<u>Cr Deposition (kg/m²)</u>
1. As cold rolled, annealed	0.17 (0.18)*
2. As 1 with oil film	0.19 (0.18)*
3. Chemical pickle	0.15
4. Sand blasted (100 mesh SiO ₂)	0.14
5. 80 grit finish	0.14

* Repeat experiments.

2.3 Process Variable Studies

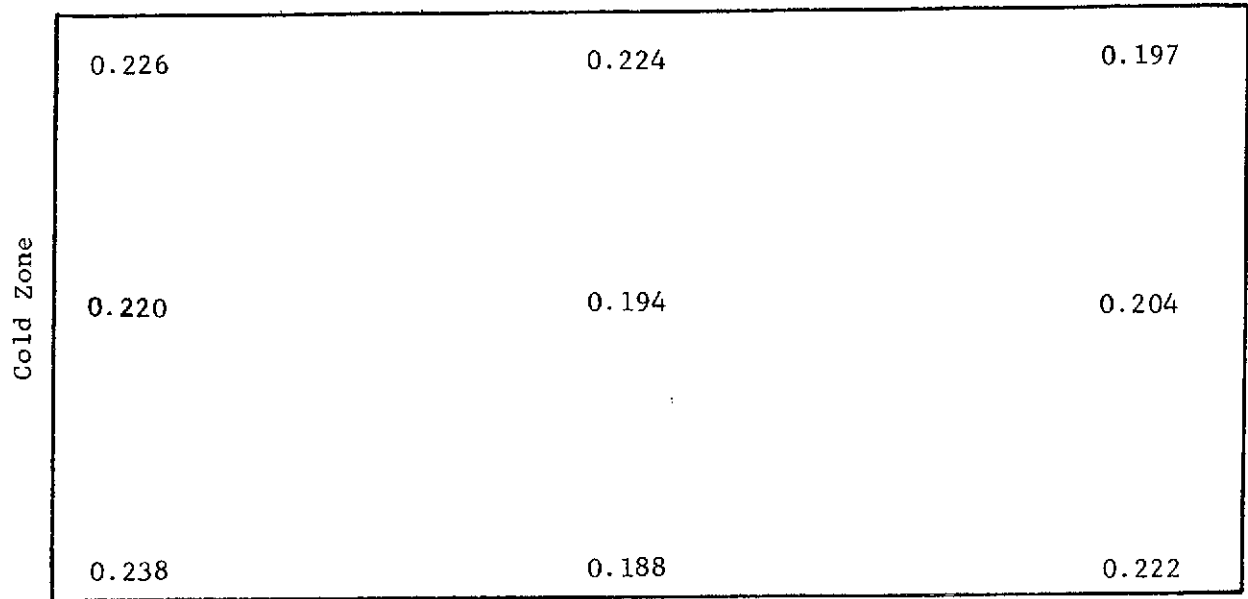
2.3.1 Preliminary Studies

The first few furnace cycles were designed to yield a measure of the temperature uniformity of the hot zone at temperatures of 1477 and 1533 K. A full-size Ni-ThO₂ sheet and nine Ni-ThO₂ coupons, 0.38 x 51 x 51 mm, spaced in three transverse rows were placed in the chromizing retort. The coupons were positioned about 50 mm from the edges of the sheet being chromized and weight changes were measured following 18 h at 1477 K and 7 h at 1533 K. The results are presented in Figure 13 and it is apparent that for a cycle of 7 h at 1533 K the temperature at the center of the pack lagged that at the edges. The scatter in the 1477 K data was much less ($\pm 12\%$) and was similar to that obtained in Task I experiments ($\pm 10\%$). At both temperatures the overall weight gain of the 0.38 x 635 x 1270 mm sheet was about equal to the lowest value shown by the individual coupons (values for the sheet were 0.178 and 0.062 kg/m² for the 1477 and 1533 K cycles respectively). This could have been caused by either:

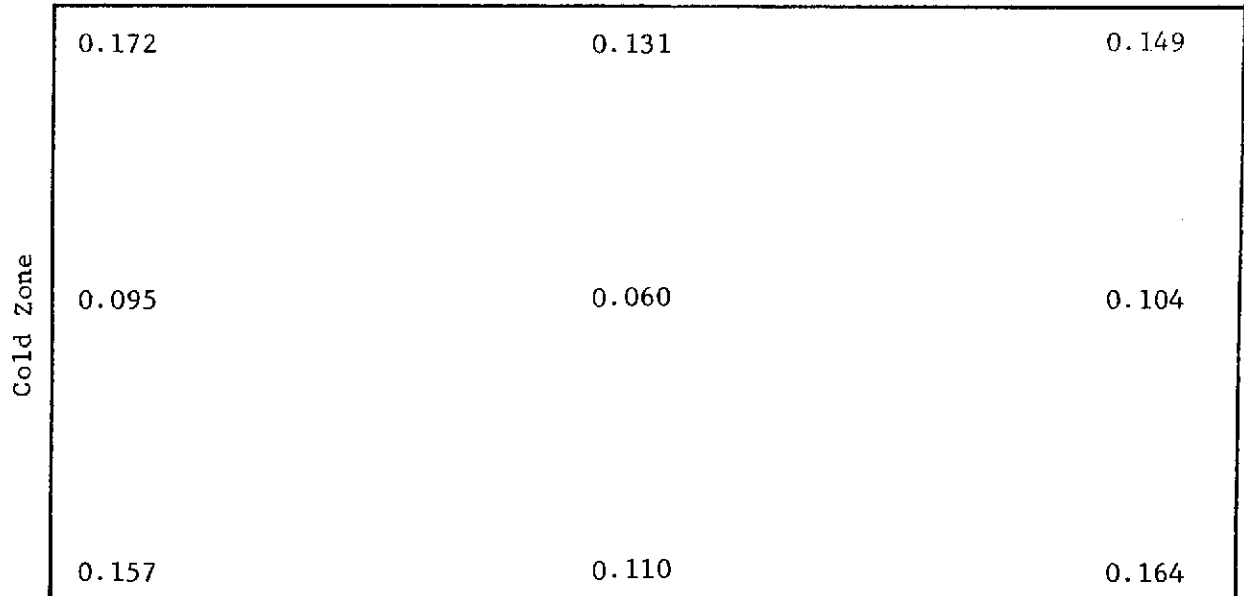
1. Vertical temperature gradients in the pack which would give greater chromizing rates near the pack surface (the coupons were about half-way between the sheet and the pack surface).
- or
2. Horizontal temperature gradients which would result in the greater part of the sheet being exposed to the lower temperature (as represented by the center coupons).

The next six cycles (FC-3 through FC-8) were used to generate chromizing rates at 1477 K for times up to 72 h using a repacking procedure. The repacking procedure consisted of removing the sheet(s) and chromizing powder from the retort, inverting the sheet(s) and returning them to the retort in the reverse stacking sequence. At least two sheets per pack were used (five sheets in FC-8) and duplicate cycles were run to give the data shown in Figure 14. The sheets were more warped than in Task I and it was probably that distortion of the chromizing retort during thermal cycling was the major contributing factor.

Cycles 9 through 14 were used to determine the hot zone uniformity and the chromizing rates at 1533 K for Ni-ThO₂ sheets from Lots 1 and 2. The chromizing rates are given in Figure 15 and show that Lot 2 Ni-ThO₂ sheets (fine grain) chromized faster than the coarse grain Lot 1 material. However, the extrapolated time to reach a 20% chromium level for each lot was about 12 h longer than that which was required in the laboratory. This increase in chromizing time was probably due to the longer heat-up times required in the scaled-up version of the process.



(a) 18 h at 1477 K



(b) 7 h at 1533 K

FIGURE 13. WEIGHT CHANGE DATA (kg/m^2) AT VARIOUS CHROMIZING PACK POSITIONS FOR TWO CHROMIZING TREATMENTS

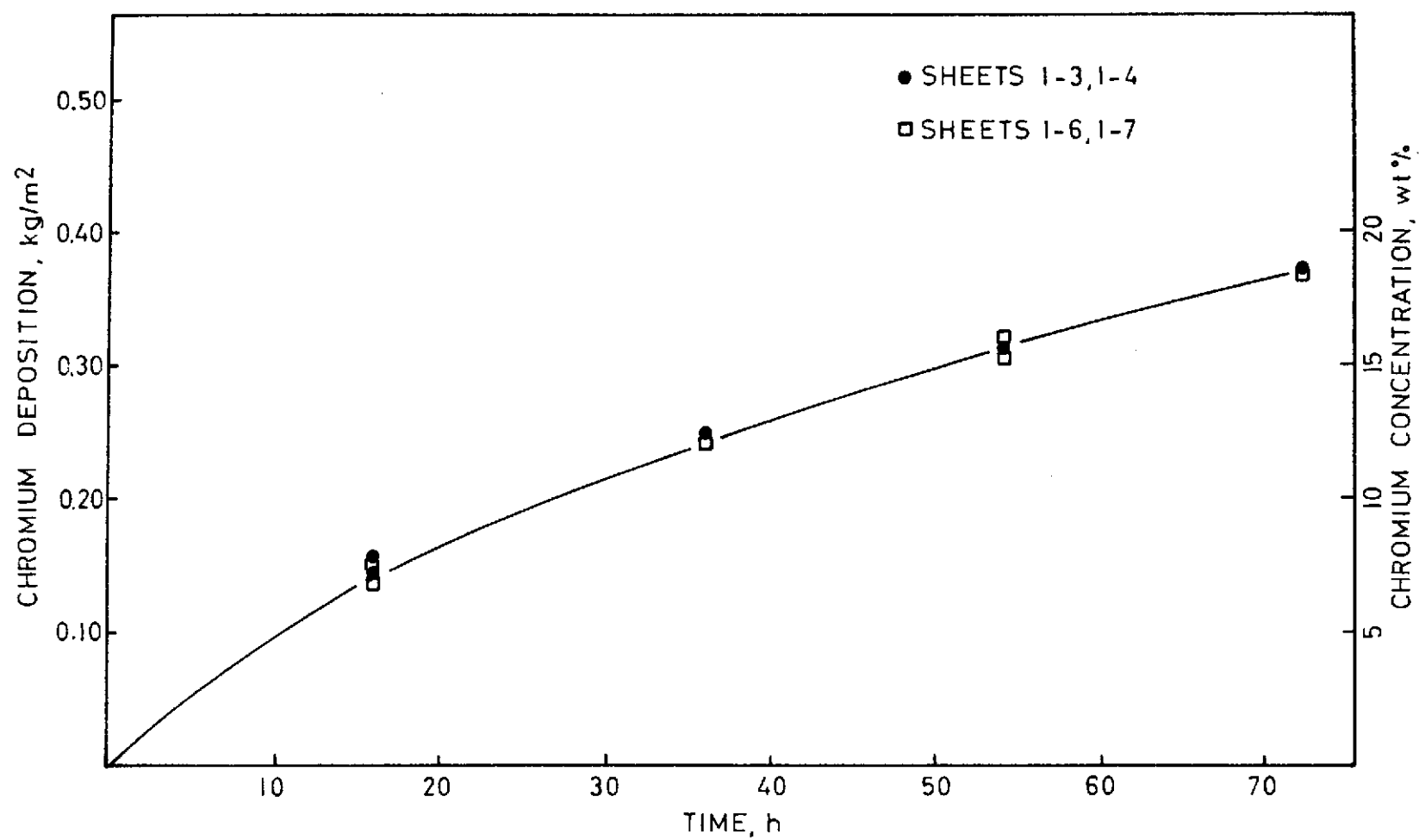


FIGURE 14. CHROMIZING RATE AT 1477 K USING REPACKING TECHNIQUE; APPROXIMATELY 16 h PER CYCLE

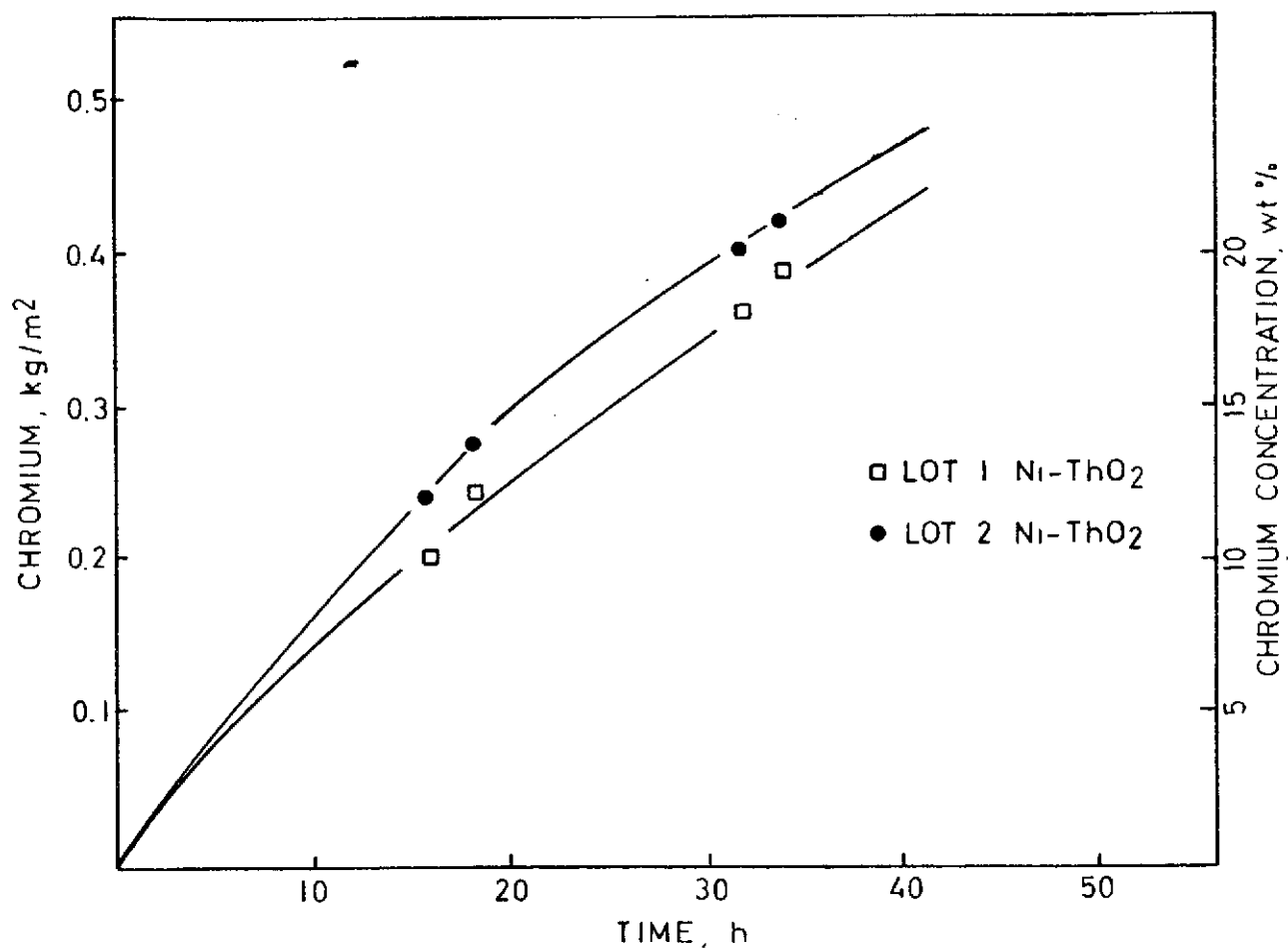


FIGURE 15. CHROMIZING RATE AT 1533 K USING REPACKING TECHNIQUES;
16 to 18 h PER CYCLE

The effect of repacking on the uniformity of chromium deposition was studied using coupons distributed throughout the chromizing pack. After 16 h at 1533 K the coupons were repacked in the standard manner (rotation about the longitudinal furnace axis) and given a second cycle of 16 h. The scatter in the data was reduced from $\pm 15\%$ for the first cycle to $\pm 10\%$ after the second. As with earlier studies the lowest deposition rate was measured at the center of the pack. Chromizing rates were higher near the top of the pack but this gradient was less than the edge-to-center horizontal gradient and was therefore easily accommodated by a top-to-bottom repacking procedure.

Chemical analyses of samples from as-chromized Sheet 2-1 (Lot 2 Ni-ThO₂) gave the overall distribution shown in Figure 16. The mean value as calculated from 45 analyses was 19.3% Cr and was in good agreement with the 19.0% Cr determined by weight gain. These data were encouraging since they described essentially the same distribution observed in the Task I feasibility studies.

An alternative approach to chromizing was also studied. Since only the bottom surface of the sheet was prone to severe separation from the chromizing pack, it was proposed to chromize one side of a sheet (the topside) at a time and thereby improve the uniformity of the chromium deposit. To test this, Sheet 1-5 was included in cycles FC-4 through FC-8 but was placed at the bottom of the pack so that alternate sides were chromized in each of the five cycles. Data on thickness variations of the as-chromized sheets were obtained and are presented statistically in Figure 17. Both distributions were skewed but in opposite directions. The standard process produced the expected low chromizing rates at the edges (due to separation) and hence had more area below the mean thickness. In the alternative process, chromium powder flowed under the sheet edges producing an apparent higher chromizing rate at these edges as shown in the bi-modal tendency of the distribution curve. Improved masking of the side that was not being chromized might have eliminated this behaviour.

2.3.2 Effect of Preheat Schedule

Determination of the optimum initial preheat schedule was done using a retort made of 1.6 mm thick mild steel and a chromizing temperature of 1533 K conducted in two cycles of 16 h each. The three preheat schedules that were evaluated were as follows:

1. Following charging, full power to 1533 K (the same that was used in all previous cycles).
2. Following charging, no power for 0.5 h, then full power to 1533 K.
3. Following charging, no power for 0.5 h, then a staged heat-up to 1533 K with 2 h dwells at 1422 K and 1477 K.

The objective was to determine if a slower heating rate to the chromizing temperature would reduce the edge-to-center chromium gradient that was observed for previous cycles. One sheet, 635 x 1370 mm, and six coupons of Lot 1 DS Ni were used for each scheme and these were repacked with a side-to-side rotation for a second 16 h cycle. Duplicate coupons were placed at three positions on a transverse line through the pack - representing the two edges and the center of the pack. Chromium weight gain data on the coupons are shown in Table XI.

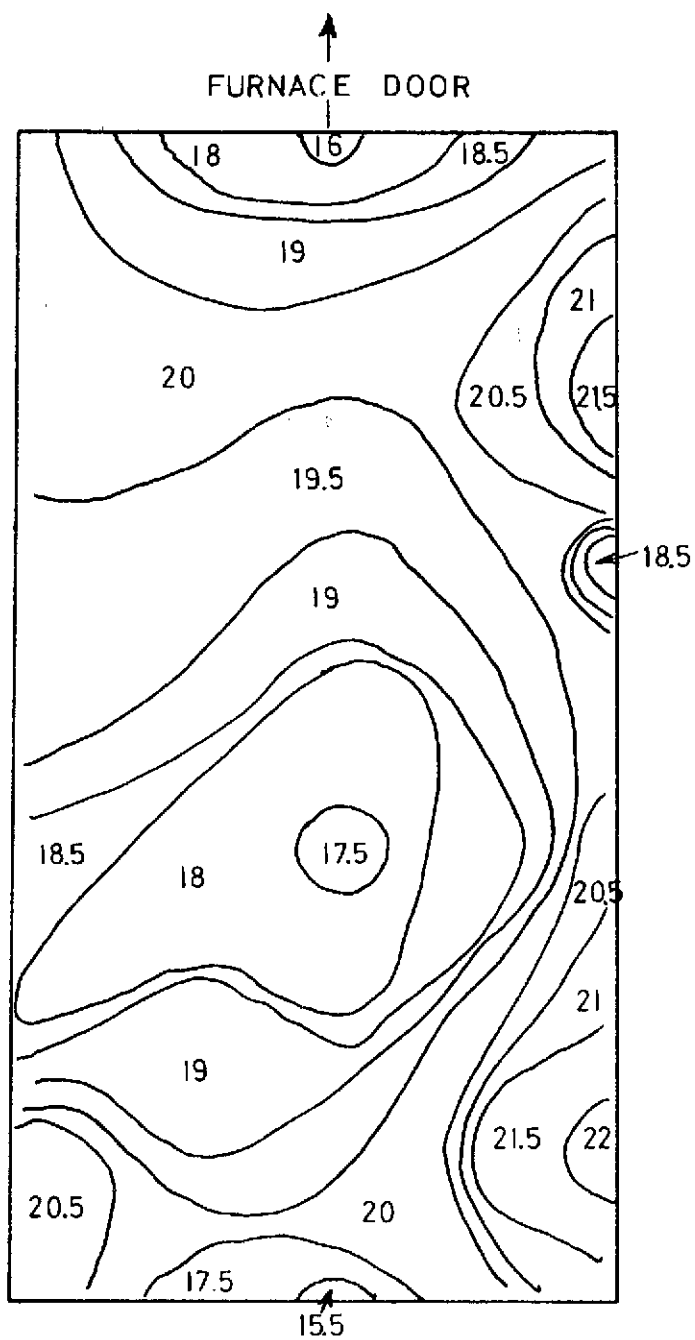
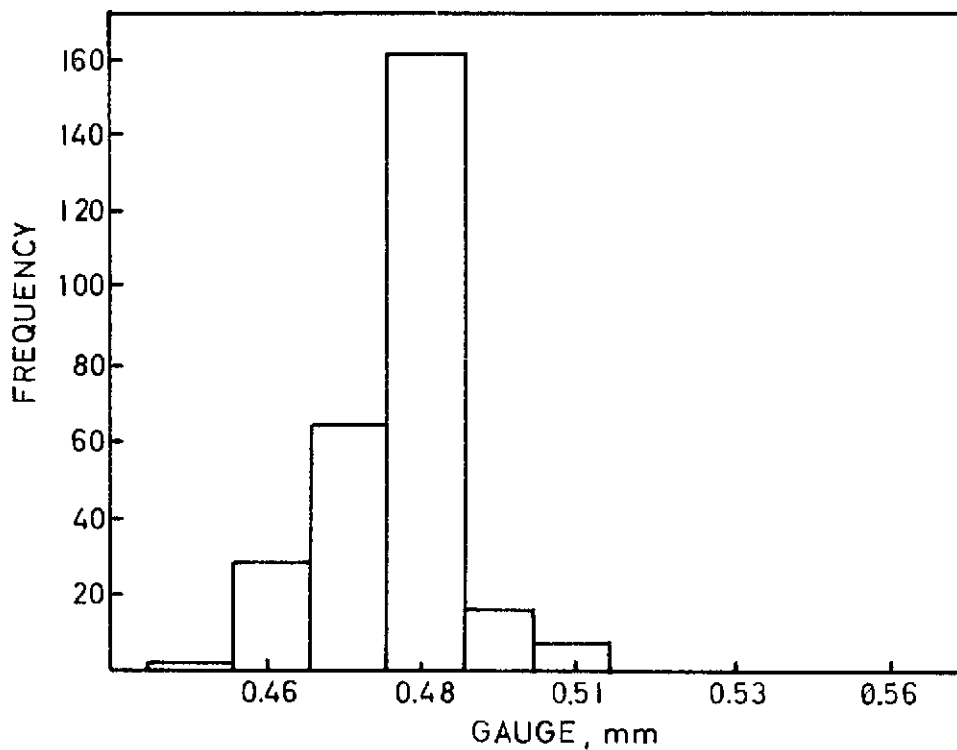
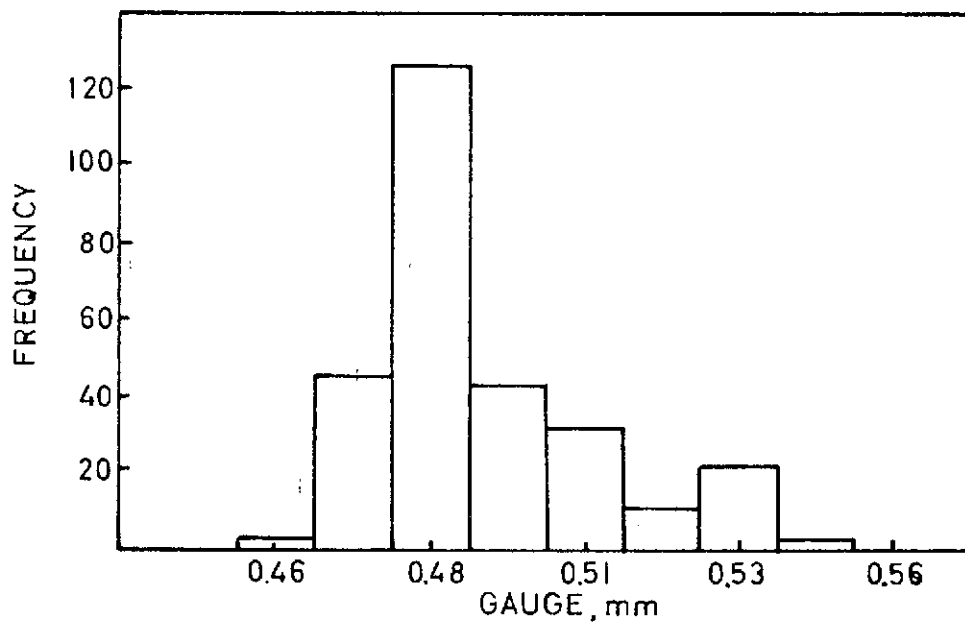


FIGURE 16. CHROMIUM DISTRIBUTION (WEIGHT PERCENT) FOR SHEET 2-1
CHROMIZED 32 h AT 1533 K. SHEET SIZE IS 635 x 1270 mm.



(a) Standard Process; Sheet 1 - 3, nominal composition Ni-16Cr-2ThO₂ (measurements to nearest 0.01 mm)



(b) Alternative Process; Sheet 1 - 5, nominal composition Ni-14.5Cr-2ThO₂ (measurements to nearest 0.01 mm)

FIGURE 17. GAUGE VARIATIONS IN AS-CHROMIZED SHEET

TABLE XI. EFFECT OF PREHEAT SCHEDULE ON THE UNIFORMITY OF CHROMIUM DEPOSITION

Coupon Positions		Preheat Schedule					
		1		2		3	
		% Cr	kg/m ²	% Cr	kg/m ²	% Cr	kg/m ²
Edge	1	17.4	0.376	19.6	0.421	18.5	0.413
	2	19.5	0.432	19.5	0.419	19.1	0.431
Center	1	20.3	0.458	19.9	0.437	18.8	0.426
	2	19.6	0.444	19.7	0.430	18.6	0.421
Edge	1	17.7	0.385	20.0	0.440	18.4	0.413
	2	17.7	0.388	18.8	0.413	18.6	0.424
Mean Value		18.7	0.414	19.6	0.427	18.7	0.421
Range (%)		±8	±10	±3	±3	±2	±2

The scatter determined in the chromium content data for schedule 1 (maximum power) compared well with the ±10% range determined in early experiments and it was obvious that slower heat-up rates reduced this range. Another very significant point was that the center coupons did not show the lowest chromium pick-up as had been the case for previous tests. This presumably was due to improved heat transfer resulting from the use of light gauge retorts rather than the earlier 4.8 mm plate retort. As schedule 3 did not contribute a significant improvement over schedule 2, the latter was selected for incorporation in the standard procedures.

2.3.3 Effect of Retort Material

A second set of experiments using different retort materials was based on comparing the behaviour of Inconel 600, RA 330 and mild steel retorts during similar furnace cycles. Retorts made of 1.6 mm Inconel 600 and RA 330 were used with preheat schedule 2 for two 16 h cycles at 1533 K. Both of the superalloy retorts distorted more than the mild steel during heating (and presumably during cooling as well). This behaviour resulted in non-uniform chromium deposition on the sample coupons in each experiment. The compositional range in the sample coupons after two cycles was ±9% for each of the superalloy retorts compared to the ±3% obtained using the mild steel retort. On this basis, as well as on a materials cost basis, the mild steel retort was selected for further experiments.

2.3.4 Multiple Sheet Chromizing

In preliminary experiments (Section 2.3.1) up to five sheets per pack were chromized but since a less-than-optimized retort design was used, the results were confounded. In addition, Lot 1 Ni-ThO₂ sheets were used and these were not so flat as Lot 2 or Lot 3 sheets. The multiple sheet experiment was therefore repeated using four 0.41 mm Lot 3 sheets and the thin gauge mild steel chromizing retort. Separation between the sheets was nominally 13 mm of powder with a top layer of about 18 mm covered by a 6.4 mm thick steel lid. Two 16 h cycles at 1533 K (actually about 1562K because of temperature control difficulties) were used with a top-to-bottom position change and end-for-end rotation of the sheets between cycles to provide the optimum chromium deposition. The results from this experiment were excellent: the sheets showed minimum distortion and had chromium depositions between 0.442 and 0.457 kg/m² which related to chromium concentrations between 19.2 and 19.5%.

2.3.5 Effect of Ni-ThO₂ Sheet Thickness

Sheets of different thickness were processed using multiple cycles of nominally 16 h at 1533 K. All sheets were processed singly. The 0.51 mm material was chromized both with and without a heavy lid on the pack to determine if increased loading would minimize sheet distortion. The data are shown in Figure 18 and confirmed the Task I conclusion that the chromizing rate per unit area was independent of sheet thickness. The abrupt change in the chromizing rate between the second and third cycles for Sheet 2-16 was caused by a faulty temperature control circuit which increased the temperature by about 14 to 28 K for the third cycle. There was no effect of the heavy lid on either the chromizing rate or the flatness of the as-chromized sheet.

2.3.6 Suitability of Other Ni-ThO₂ Sheet Stock

The purchase of Ni-ThO₂ sheet material included two sheets of 0.38/0.46 mm TD Ni (Lot 2A) and two sheets of 0.38 mm unannealed DS Ni. Chromizing and homogenizing of these two different materials was completed but the hoped-for improvement due to better visual flatness was not observed. The chromizing rates were equivalent and were only slightly greater than those for Lot 2 or Lot 3, 0.38 mm DS Ni.

2.3.7 Homogenizing Studies

Ten chromized sheets were given a homogenizing anneal of nominally 40 h at 1533 K. Of particular interest in these studies was the construction of the annealing pack: number of sheets per pack, requirement for a parting agent between the sheets and the effect of added weights on the tendency of the sheets to flatten out during the anneal. The following conclusions were made in these three areas:

- At least six sheets could be annealed together without difficulty.

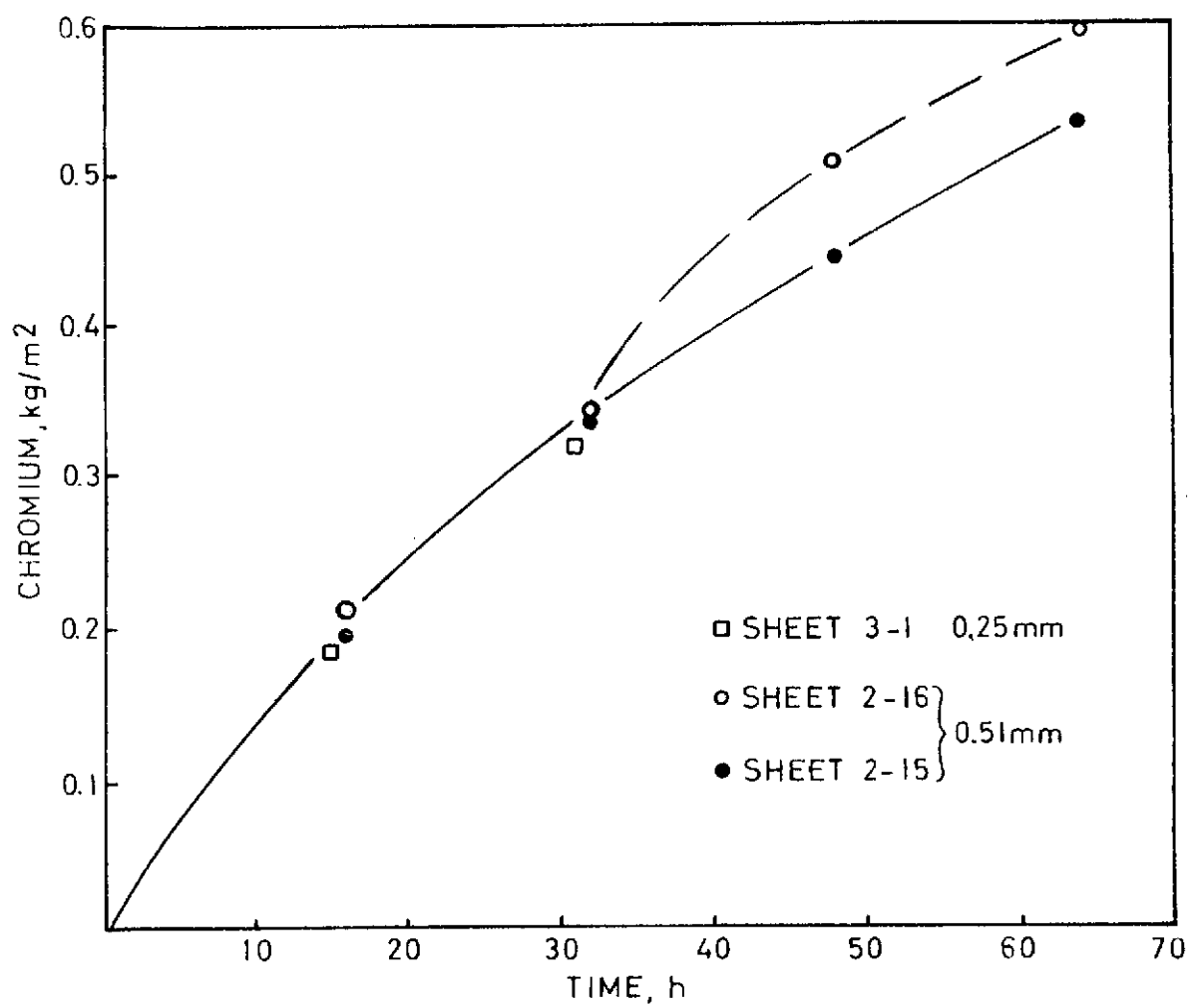


FIGURE 18. CHROMIZING RATES AT 1533 K FOR 0.25 AND 0.51 mm Ni-ThO₂ SHEET

- Residual oxide powder on the surface of the as-chromized sheets was sufficient to prevent sticking of the sheets. Other powders (MgO , Cr_2O_3 and yttrium nitrate) also prevented sticking but resulted in a type of surface oxidation.
- Loading ranging from about 96 N/m^2 up to 1150 N/m^2 had little measurable effect on the flatness of the sheet. Sheets annealed under the higher loading "looked" flatter but this was not confirmed by quantitative analysis.

2.3.8 Sheet Leveling Studies

Six sheets of 0.38 mm Lot 2 Ni-ThO₂ were processed to provide material for sheet flattening and wide belt abrasive grinding studies. A mild steel retort, the #2 preheat schedule, two sheets per pack and two cycles at 1533 K were used to process the sheets. The sheets were repacked for the second cycle using a top-to-bottom position change and rotation about the longitudinal furnace axis. (Note that an improved process was determined in Section 2.3.4: four sheets per pack and a rotation about the transverse furnace axis.) The overall chromium concentration for these sheets was between 18.8 and 19.8% Cr which related to depositions of from 0.402 to 0.415 kg/m². On the basis of the chromium concentration profiles generated earlier in the programme (Figure 16) the average chromium levels obtained for these sheets were too low to guarantee that no area on the sheet contained less than 18% chromium. However, this material was destined primarily for the evaluation of flattening techniques and gauge control on the subsequently ground product and a slightly low overall chromium concentration was not expected to affect the proposed study. (A minor adjustment in either chromizing temperature or time provided material with higher average chromium concentrations in subsequent chromizing runs.)

The six sheets were annealed for 40 h at 1533 K to reduce the surface-to-center chromium gradients. The annealing pack consisted of nickel waster sheets top and bottom with 6.4 mm thick steel plates providing a total surface loading of about 570 N/m^2 .

Studies in Task I had indicated that flatness was an important parameter in the surface grinding operation. Since the quality of the larger sheets in Task II was expected to be even more sensitive to flatness, considerable effort was devoted to determine that sensitivity. Three techniques to level the annealed sheets were considered: roller leveling, stretcher leveling and tension cold rolling. Stretcher leveling was done at the Cyril Bath Co. in Cleveland, Ohio, and the roller leveling and cold rolling were done at the (then) Refractory Metal Rolling Operation of the General Electric Co. also in Cleveland, Ohio. The homogenized sheets were qualitatively ranked for initial flatness and two sheets, one from each end of the flatness range, were processed through each of the three leveling routes. A summary of the processing is given in Table XII.

TABLE XII. PROCESSES USED IN THE SHEET LEVELING STUDY

Process	Sheet Numbers	Starting Flatness ^a	Description of Process	Final Flatness ^a and Recovery ^b
Roller Leveling	2-3	2	Three passes using 127 mm diameter rolls. Four passes on 51 mm rolls.	Flatness 1 Recovery 100%
	2-8	1	Same	Flatness 1 Recovery 100%
Stretcher Leveling	2-9	1	Permanent strain 0.4%	Flatness <1 Recovery 96%
	2-10	2	Permanent strain 2.4%	Sheet broke before desired flatness achieved. Recovery 92%
Tension Cold Rolling	2-4	3	7% reduction on 305 mm diameter rolls.	Flatness <<1 Recovery 83%
	2-7	2	6% reduction on 305 mm diameter rolls.	Flatness <<1 Recovery 81%

a. Qualitative Ranking: 1 is good, 3 is poor.

b. After shearing grip marks from sheet.

The results indicated that roller leveling did not produce the permanent strain necessary to improve the flatness of the sheet, possibly because the yield stress of the alloy (about 620 MN/m²) exceeded the designed capacity of the roller leveling unit. The stretching operation removed all of the major edge waves in the sheet but there were many low amplitude (less than 3.2 mm), low frequency undulations still remaining throughout the sheet. Sheet 2-10 was the first to be stretched and flatness inspection was achieved by removing the sheet from the stretching unit at various strain intervals. Misalignment during regripping may have been responsible for sheet breakage during stretching and for the apparent inability to achieve the desired flatness. The second sheet, 2-9, was stretched to good visual flatness in a single step and with a much lower permanent strain. The tension cold rolling produced sheet that was essentially "dead flat" but resulted in low final sheet recovery due to unavoidable tension end losses.

2.3.9 Sheet Grinding Studies

The surface grinding was done at the Hill Acme Co. in Cleveland, Ohio, using conditions established in Task I experiments, namely: use of coolant with 80 grit SiC belts, 12.7 m/s belt speed, 0.03 m/s feed stock speed and double sided masking tape to hold the sheets to a carrier plate (3.2 mm hardened Al sheet). A summary of the results of the processing is given in Table XIII.

TABLE XIII. SUMMARY OF SURFACE FINISHING DATA

Sheet ^a	Number of Passes	Total Stock Removal mm	Final Gauge ^b mm	Surface Finish ^c RMS, nm
RL-2-3	15	0.114	0.396	not determined
RL-2-8	24	0.084	0.368	380/710
SL-2-9	20	0.104	0.394	320/380
SL-2-10	18	0.099	0.394	320/410
TCR-2-4	14	0.079	0.386	360/510
TCR-2-7	16	0.102	0.348	380/380

a. RL - roller leveled; SL - stretcher leveled; TCR - tension cold rolled.

b. Micrometer readings at sheet edges.

c. Slash (/) separates readings from each side of sheet.

The number of passes on a new belt determined the stock removal per pass as well as the resulting surface finish. Belts were replaced every 15 to 20 passes and a used belt was used for the last two passes on each sheet to provide a reasonably uniform surface finish (with the exception of the first three sheets processed: 2-3, 2-8 and 2-4).

2.4 Physical and Mechanical Properties

2.4.1 Gauge Control and Flatness

Thickness measurements were made on a 127 mm grid over the entire sheet using an ultrasonic digital thickness gauge. Flatness was measured, also on a 127 mm grid, as the height of the sheet surface (at a grid intersection) above a flat reference surface. Contour maps of the flatness could be generated but for the purpose of a single number ranking system the height measurement was related to an integral number as follows:

<u>Height (mm)</u>	<u>Ranking</u>
less than 3.2	0
3.2-6.35	1
6.4-12.7	2

The integral numbers from all the grid intersections were then added to give a value for "Flatness". A simple percentage flatness as determined by the conventional H/L method (where H is the maximum height above the reference surface and L is the shortest horizontal distance to a point of contact with the reference surface) was also calculated for all sheets. As a further characterization of the gauge control obtained, the theoretical nominal weight of

each sheet was calculated (for nominally 20% Cr and 0.38 mm sheet thickness) and compared to the actual sheet weight. These data are given in Table XIV. Figure 19 shows the effect of the different leveling procedures on the appearance of the sheets.

TABLE XIV. GAUGE CONTROL AND FLATNESS DATA

Sheet Number	Flatness		Sheet Thickness, mm			Theoretical Nominal Sheet Weight kg	Actual Sheet Weight kg	% Deviation from Nominal
	INR ^a	%	Min.	Max.	Total Variation			
RL-2-3	11	5.4	0.366	0.419	0.053	2.55	2.72	+6.7
RL-2-8	61	11.5	0.333	0.381	0.048	2.54	2.46	-3.2
SL-2-9	7	3.9	0.371	0.419	0.048	2.43	2.51	+3.3
SL-2-10	16	3.9	0.368	0.424	0.056	2.36	2.47	+4.7
TCR-2-4	0	4.2	0.354	0.412	0.058	2.27	2.31	+1.8
TCR-2-7	0	2.5	0.315	0.368	0.053	2.20	2.04	-7.3

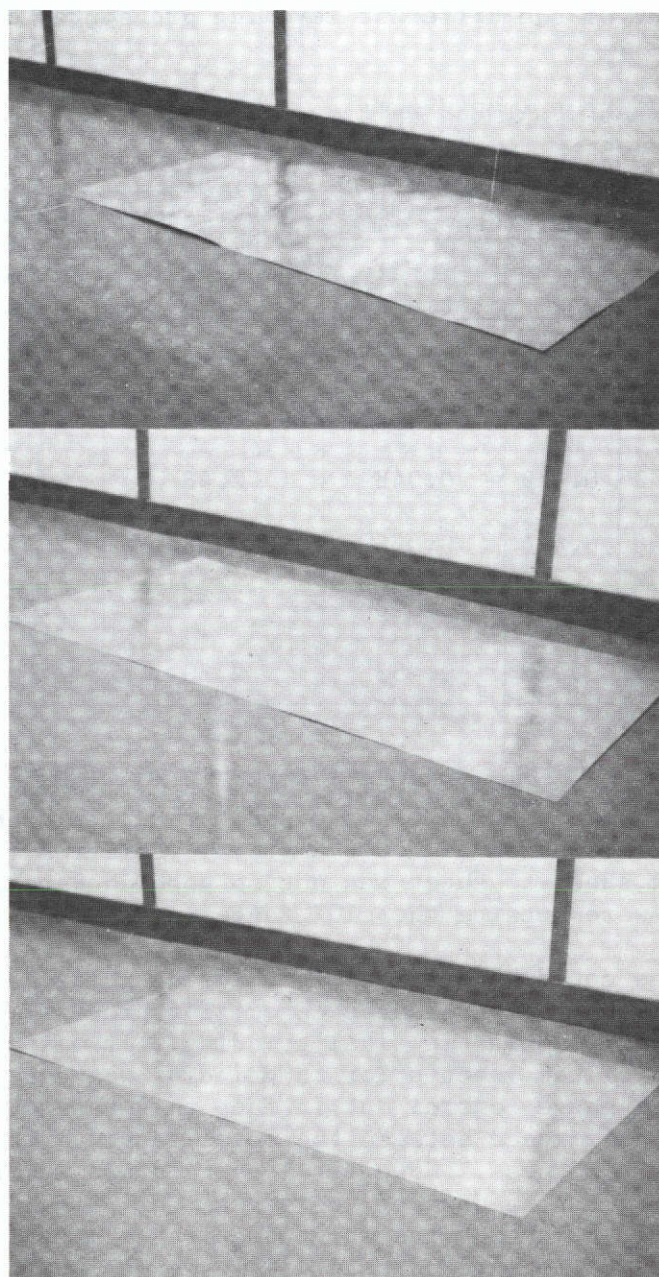
a. Integral Number Ranking.

Gauge control within each sheet was good and all thickness measurements were within the specification of 0.076 mm total variation for 0.38 mm material. Variation from sheet to sheet was not so good, however, as several sheets had regions which were outside the $\pm 10\%$ range (i.e. 0.343 to 0.419 mm).

Gauge variations could have arisen in three basic areas of the process: in the starting Ni-ThO₂ sheet, in the chromizing process (due to non-uniform chromium deposition) and in the final grinding. It was originally thought that the flatness of the sheet prior to grinding would be a controlling factor in the ultimate gauge control but in fact this was not the case as there was no significant difference between the total gauge variations in sheets with widely varying flatness. However, a certain minimum flatness was necessary to facilitate the taping down of the sheets for grinding. In this respect, the roller leveled stock was the only undesirable material. The appearance of the cold rolled and ground material was excellent and the aesthetic quality of the stretcher leveled sheets was marred only by the previously described low amplitude undulations. Flatness, then, appears to affect only the appearance of the final product.

2.4.2 Mechanical Properties

Tensile properties were measured on surface-ground samples from each of the three leveling processes and are given in Table XV. The room temperature data reflect the various degrees of strain imposed during the leveling



a) Roller leveled
Sheet 2-3

b) Stretcher leveled
Sheet 2-9

c) Tension Cold Rolled
Sheet 2-7

FIGURE 19. EFFECT OF DIFFERENT LEVELING PROCEDURES ON FLATNESS OF
FINAL PRODUCT SHEETS. NOMINAL SIZE OF SHEETS IS
600 x 1100 mm.

operation. Samples of the three sheets were stress-relieved for 0.5 h at 1477 K to determine if the mechanical properties could be recovered. Room temperature data for the stress-relieved samples are given in Table XVI and show that room temperature ductility was restored in TCR-2-4. The 1366 K tensile properties of the stress-relieved sheet were unchanged with the exception of the longitudinal yield strength of sheet TCR-2-4 which increased from 48 to 73 MN/m². A full size tension cold rolled sheet (TCR-2-7) was stress-relieved but flatness was lost during the anneal and no further studies were conducted.

TABLE XV. REPRESENTATIVE TENSILE PROPERTIES^a OF SURFACE GROUND Ni-Cr-ThO₂ SHEET

Sheet Number	Room Temperature					
	Longitudinal			Transverse		
	0.2% Yield Stress MN/m ²	Ultimate Tensile Strength MN/m ²	% Elongation	0.2% Yield Stress MN/m ²	Ultimate Tensile Strength MN/m ²	% Elongation
RL-2-8	675	845	16	600	825	15
SL-2-10	760	890	15	655	810	12
TCR-2-4	880	915	8	830	885	6
1366 K						
RL-2-8	77	81	2	77	90	2
SL-2-10	74	79	2	95	100	2
TCR-2-4	48	81	2	80	95	2

- a. Elongations were measured in a 25.4 mm gauge length. At room temperature, tensile testing was done at a strain rate of $8.3 \times 10^{-5} \text{ s}^{-1}$ up to 0.6% strain followed by $8.3 \times 10^{-4} \text{ s}^{-1}$ to failure. At 1366 K strain rate was $8.3 \times 10^{-4} \text{ s}^{-1}$.

TABLE XVI. REPRESENTATIVE ROOM TEMPERATURE TENSILE PROPERTIES^a
OF STRESS-RELIEVED MATERIAL

Sheet Number	Longitudinal			Transverse		
	0.2% Yield Stress MN/m ²	Ultimate Tensile Strength MN/m ²	% Elongation	0.2% Yield Stress MN/m ²	Ultimate Tensile Strength MN/m ²	% Elongation
RL-2-8	630	800	17	625	795	15
SL-2-10	600	785	16	645	815	17
TCR-2-4	660	790	12	690	825	13

a. Elongations are measured in a 25.4 mm gauge length. At room temperature, tensile testing was done at a strain rate of $8.3 \times 10^{-5} \text{ s}^{-1}$ up to 0.6% strain followed by $8.3 \times 10^{-4} \text{ s}^{-1}$ to failure.

2.5 Selection of a Standard Process

Analysis of the results of the process variable studies indicated that the Standard Process for the production of 0.38 x 610 x 1220 mm Ni-Cr-ThO₂ sheet using the sheet chromizing process should be as follows.

2.5.1 Raw Materials

- The starting Ni-2ThO₂ sheet should have mechanical properties and physical dimensions equal to or greater than those expected for the product Ni-Cr-ThO₂ sheet. The sheet flatness should exceed the SAE specification (AMD 55 DG) of 6%.

- The chromizing pack should consist of chromium powder (-325 mesh) modified with about 5% of a suitable inert material (Y₂O₃, ThO₂). Normal precautions should be taken when handling the powder.

2.5.2 Chromizing

- The retort should be constructed of 1.6 mm thick mild steel and a heavy lid should be used which applies a loading of at least 480 N/m².

- The pack should consist of four sheets with about 13 mm of powder separating the sheets.

- The pack should be charged into a soaked-out furnace having a hydrogen atmosphere (dew point less than 233 K). Power to the furnace should be turned off for 0.5 hr following charging to allow temperature stabilization in the pack. The temperature of the charge should then be raised to the chromizing temperature at the maximum heating rate.

- Two cycles of 16 h duration at 1562 K should be used. Sheets should be inverted end for end between each cycle. Chromizing time or temperature should be modified so that each sheet shows a 20 to 21 wt. % chromium content.

2.5.3 Homogenizing

- The homogenizing pack can consist of up to at least ten sheets with an additional loading of about 960 N/m² supplied by dead weights added on top of the charge to promote flattening. Waster sheets should be used between the Ni-Cr-ThO₂ sheets and the weights to prevent contamination.

- The pack should be charged to a soaked-out furnace having a hydrogen atmosphere (dew point less than 233 K) and be held at 1562 K for a minimum of 40 h.

2.5.4 Leveling and Finishing

- The sheets should be stretcher leveled using a loading to produce between 0.5 and 2.0% permanent strain.

- The sheets should be surface finished using wet, wide belt abrasive grinding. The grinding belts should be wet bonded 80 grit SiC and should remove about 0.050 mm/side. A worn 80 grit belt should be used for the last two passes to provide a surface finish of less than 410 nm RMS.

- The ground sheets should be sheared to final product size.

2.6 Process Reproducibility

2.6.1 Processing

The Standard Process was used to produce four sheets of 0.38 x 610 x 1220 mm Ni-Cr-ThO₂ alloy in a process reproducibility trial. A summary of the chromizing data is as follows:

Sheet No.	Chromium	
	%	kg/m ²
3-15	20.3	0.455
3-16	20.4	0.473
3-17	19.6	0.467
3-18	19.6	0.457

All four sheets were stretcher leveled to good flatness. Total permanent strain varied from 1.6 to 1.8%. Surface grinding proceeded routinely. Because of an increase in thickness of the starting Ni-ThO₂ sheet (Lot 3 stock was about 0.025 mm thicker than Lot 2) the stock removal during grinding was increased to nominally 0.076 mm per side from 0.051 mm per side. A summary of the surface finishing data is given in Table XVII.

TABLE XVII. SURFACE FINISHING DATA; PROCESS REPRODUCIBILITY

Sheet No.	Number of Passes	Total Stock Removal mm	Final Gauge mm	Surface Finish RMS (nm)
3-15	32	0.152	0.381	280/280
3-16	34	0.160	0.391	280/280
3-17	32	0.157	0.389	280/280
3-18	30	0.150	0.391	250/250

2.6.2 Gauge Control and Flatness

The surface quality and general appearance of the sheets were excellent. The low frequency undulations that had marred the appearance of previous stretcher leveled sheets (Section 2.4.1) were notably absent, possibly because of the general improvement in sheet flatness that was achieved during the chromizing and homogenizing operations. Measurements of gauge and flatness were carried out on all sheets as described earlier (Section 2.4.1) and are given in Table XVIII.

TABLE XVIII. GAUGE CONTROL AND FLATNESS; PROCESS REPRODUCIBILITY

Sheet Number	Flatness		Sheet Thickness, mm			Theoretical Nominal Sheet Weight kg	Actual Sheet Weight kg	% Deviation from Nominal
	INR	%	Minimum	Maximum	Total Variation			
3-15	32	4.5	0.343	0.411	0.068	2.41	2.50	+3.7
3-16	18	4.2	0.384	0.424	0.040	2.41	not obtained	
3-17	29	5.7	0.366	0.422	0.056	2.41	2.55	+5.8
3-18	23	3.1	0.373	0.432	0.059	2.41	2.60	+7.9

Comparison of the above data with those for the two stretcher leveled sheets in the process variable studies (Table XIV) showed good agreement. The mean thicknesses of the sheets, however, were higher for the process reproducibility sheets and gave correspondingly higher values for the deviation from nominal weight criterion. It is believed that higher grinding loads which resulted in deflection of the rubber contact roll were responsible for an increased stock removal at the sheet edges. The resulting taper in the outer 50 to 75 mm of the sheet was not detected during processing nor was it expected, based on the earlier surface finishing trial.

2.6.3 Evaluation of Mechanical Properties and Chemical Composition

Sheet 3-16 from the process reproducibility trial was tested for mechanical properties and uniformity of chromium. Samples were taken randomly from different areas on the sheet for tensile testing and from a 127 mm grid system for wet chemical analysis of chromium concentration. The mechanical property data are shown in Table XIX; these data essentially reproduced those which had been measured in the process variable studies (Section 2.4.2).

TABLE XIX. MECHANICAL PROPERTIES OF REPRESENTATIVE MATERIAL FROM PROCESS REPRODUCIBILITY TRIAL (SHEET 3-16)

Mechanical Properties	Longitudinal	Transverse
<u>Room Temperature</u>		
0.2% Yield Strength, MN/m ²	685	630
Ultimate Tensile Strength, MN/m ²	850	835
% Elongation in 25.4 mm	16	17
<u>1366 K</u>		
0.2% Yield Strength, MN/m ²	70	77
Ultimate Tensile Strength, MN/m ²	85	92
% Elongation in 25.4 mm	2	2
<u>Bend Test</u> , 105° around 2t radius	pass	pass

Wet chemical analyses from 60 locations in Sheet 3-16 gave a mean chromium concentration value of 19.6%. Three areas had less than the 18% Cr minimum target level, the lowest being 17.1%. Additional analytical data are given in Table XX.

TABLE XX. CHEMISTRY^a OF REPRESENTATIVE MATERIAL FROM PROCESS REPRODUCIBILITY TRIAL (SHEET 3-16)

Cr	Mn	Fe	C	S	ThO ₂	Excess O ₂
17.1-21.8	0.08	0.11	0.006	0.012	1.72	0.03

a. Values are in weight percent.

Mechanical properties of sheet 2-13 (processed from TD Ni sheet) were also determined and are reported in Table XXI. The differences in the properties of the two sheets were attributable to differences in the properties of the starting Ni-ThO₂ material (see Table IX).

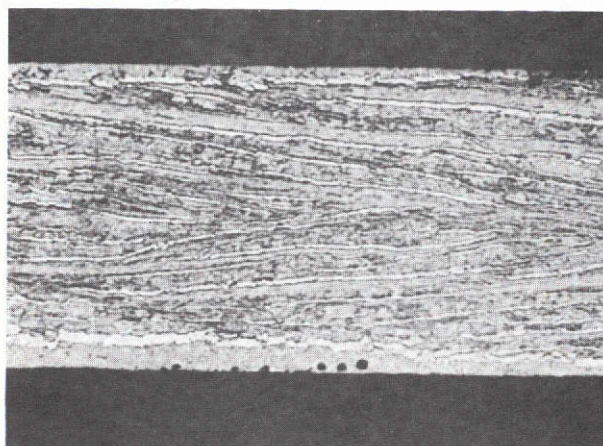
TABLE XXI. MECHANICAL PROPERTIES OF SHEET 2-13 (0.38 mm)

Mechanical Properties	Longitudinal	Transverse
<u>Room Temperature</u>		
0.2% Yield Strength, MN/m ²	625	620
Ultimate Tensile Strength, MN/m ²	790	745
% Elongation in 25.4 mm	14	16
<u>1366 K</u>		
0.2% Yield Strength, MN/m ²	90	103
Ultimate Tensile Strength, MN/m ²	99	112
% Elongation in 25.4 mm	3	4
<u>Bend Test</u> , 105° around 2t radius	pass	pass

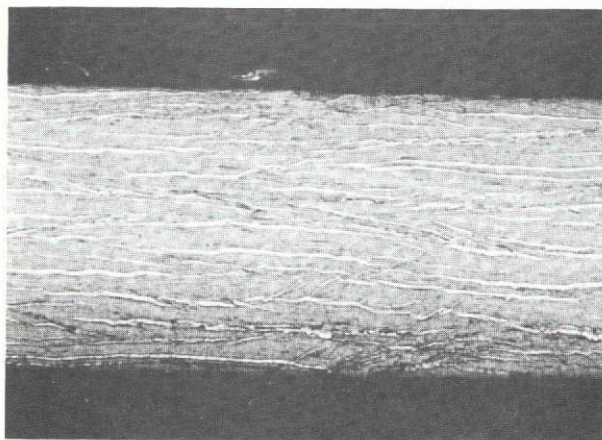
Representative microstructures of transverse sections of Sheets 3-16 and 2-13 are shown in Figure 20. The familiar ThO₂-free zones are apparent in both microstructures and generally reflect the locations of original Ni-ThO₂ grain boundaries parallel or nearly parallel to the sheet surface. Transmission electron micrographs of samples from sheets 3-16 and 2-13 are given in Figure 21. Figure 22 shows the presence of a ThO₂-free area. With the exception of the ThO₂-free areas, the microstructures of the chromized and homogenized sheets were similar to those of the starting sheets. The apparent difference in ThO₂ size distribution between sheet 3-16 and 2-13 was also characteristic of the starting sheets.

A series of stress rupture tests was conducted on material prepared in the process reproducibility trial. As shown in Figure 23 the material possessed a 100 h life at 1366 K of about 34.5 MN/m² but also showed elongations at failure of up to 80%. Closer examination of this phenomenon showed that these high values were misleading in that material failure had actually occurred much earlier in the test and that the stress/strain rate conditions were such that the oxide which formed in the failed region had sufficient strength to delay overall failure for a considerable length of time. The elongation at the point of initial failure was in the range 1 to 3% which was typical of other material processed in this programme. Without the effect of the oxide the 100 h life would likely have been about 27 MN/m² (determined by estimating the time at which the strain exceeded about 3% for each test and plotting a new stress-time relationship).

This phenomenon has since been observed in TD NiCr and Whittenberger (ref. 5) has proposed a model based on diffusional creep which explains the creep rupture behaviour and the degradation of room temperature properties following high temperature creep of several dispersion strengthened alloy systems.



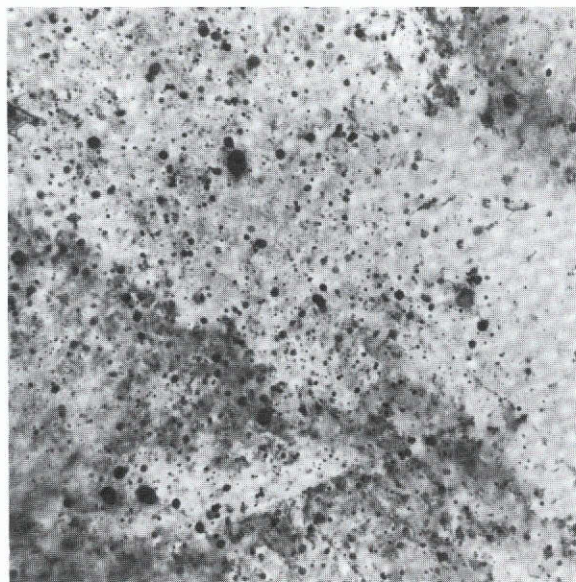
a) Sheet 3-16 (x100)



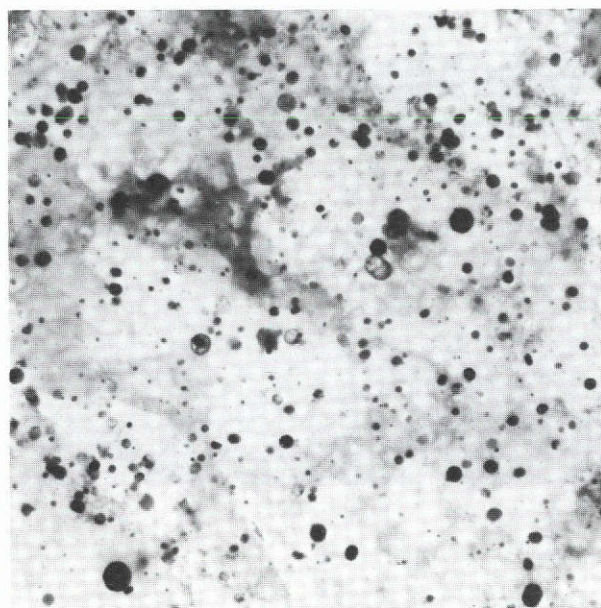
b) Sheet 2-13 (x100)

FIGURE 20. TRANSVERSE MICROSTRUCTURES OF Ni-Cr-ThO₂ SHEETS PRODUCED IN TASK II; ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

TRANSMISSION ELECTRON MICROGRAPHY
PRODUCED IN TASK II (x20)



a) Sheet 3-16



b) Sheet 2-13

FIGURE 21. TRANSMISSION ELECTRON MICROGRAPHS OF Ni-Cr-ThO₂ SHEETS PRODUCED IN TASK II (x20,000)

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FIGURE 22. TRANSMISSION ELECTRON MICROGRAPH SHOWING ThO_2 -FREE AREA IN SHEET 2-13 (x20,000)

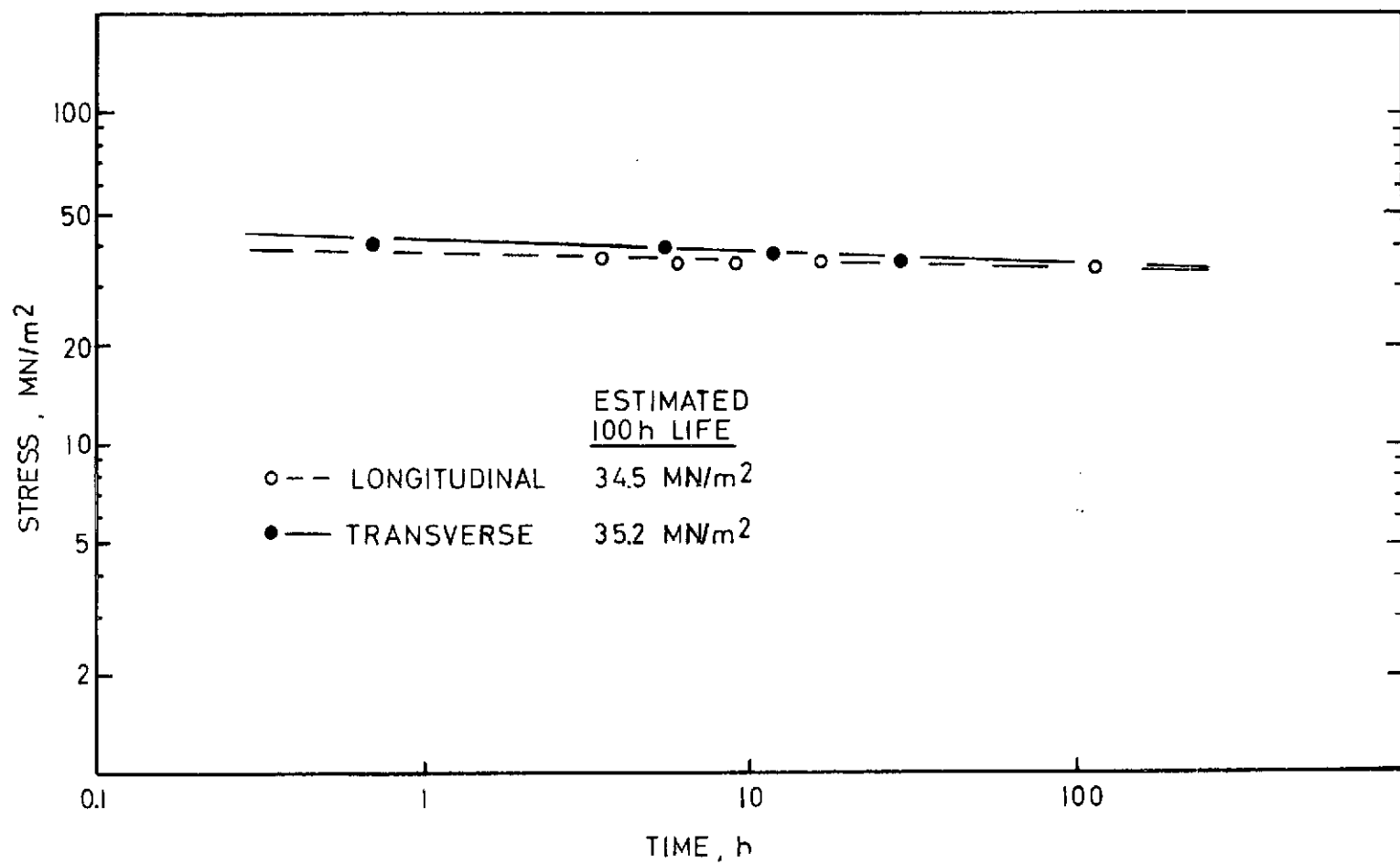


FIGURE 23. 1366 K STRESS RUPTURE PLOT FOR Ni-Cr-ThO₂ PRODUCED IN TASK II

Because of the unique nature of the structure of Ni-Cr-ThO₂ alloys produced by chromizing and homogenizing a study was conducted on the stress rupture behaviour of the various types of sheet material that were produced in the programme. A variety of grain structures was available and these are shown in Figure 24. Stress rupture data from tests at 1366 K are given in Figure 25 and indicate that higher 100 h stress levels are achieved when the ThO₂-free zones in the microstructure are aligned parallel to the applied stress direction (e.g. Sheet 5). The lowest rupture strength was measured for Sheet 3-16 which had many ThO₂-free zones inclined to the stress axis.

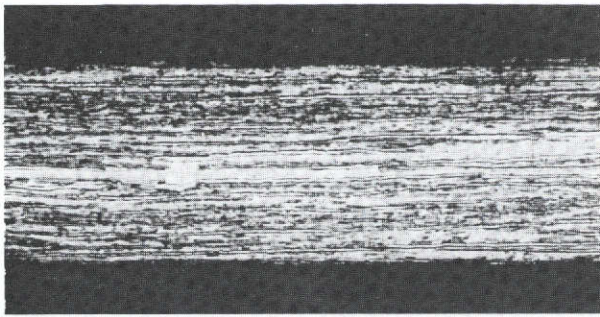
Figure 26 shows sections of stress rupture samples (some of which failed on unloading) and the failure mode is quite apparent: coalescence of voids which had formed on boundaries perpendicular to the stress axis followed by shear failure along boundaries connecting the voids. Internal oxidation in the failed region is visible in the TD NiCr sample but not in the others presumably because failure had not progressed that far in the photographed sections.

2.7 Task Completion

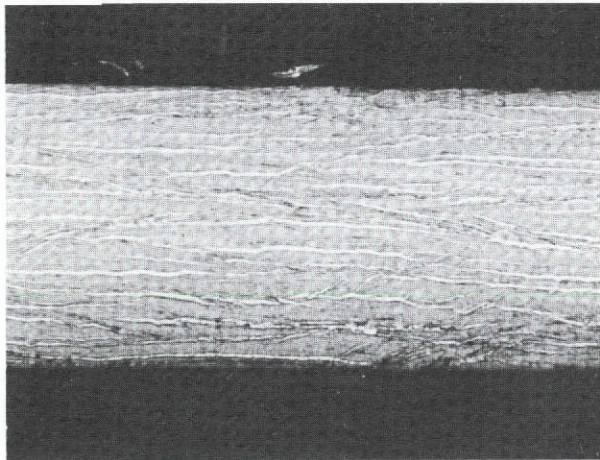
The results from the process reproducibility trial indicated that the pack chromizing and homogenizing process could produce Ni-Cr-ThO₂ sheet up to 610 x 1220 mm in the gauge range 0.25 to 0.51 mm. Elevated temperature testing, however, indicated that a particular microstructure was required to ensure adequate stress rupture properties and it was therefore recommended that the balance of the programme be conducted with TD Ni sheet rather than DS Ni. However, because of interest in an alloy with improved oxidation resistance, the scope of this project was increased to allow the study of processing conditions necessary to produce an aluminum-modified Ni-Cr-ThO₂ alloy using the basic process developed in the Task II studies.

The following Ni-Cr-ThO₂ sheets were shipped to NASA-Lewis as required for the completion of Task II:

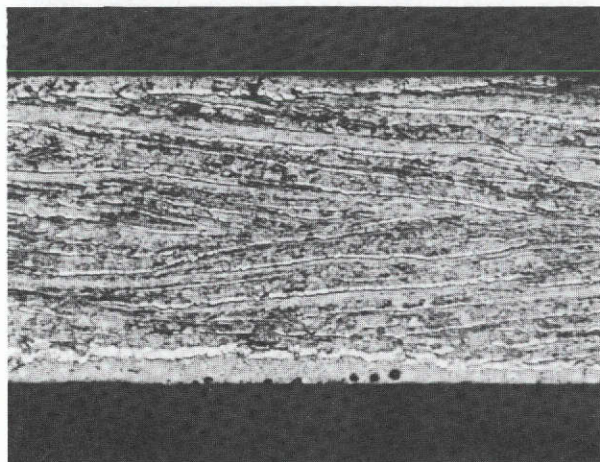
<u>Sheet No.</u>	<u>Size (mm)</u>	<u>Weight (kg)</u>
3-15	0.38 x 610 x 1220	2.5
3-17	0.38 x 610 x 1220	2.55



a) Sheet 5
(Task I DS Ni Lot 170)



b) Sheet 2-13
(Task II TD Ni Heat 3293)



c) Sheet 3-16
(Task II DS Ni Lot 3)

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FIGURE 24. MICROSTRUCTURES OF VARIOUS Ni-Cr-ThO₂ ALLOYS (x100)
ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

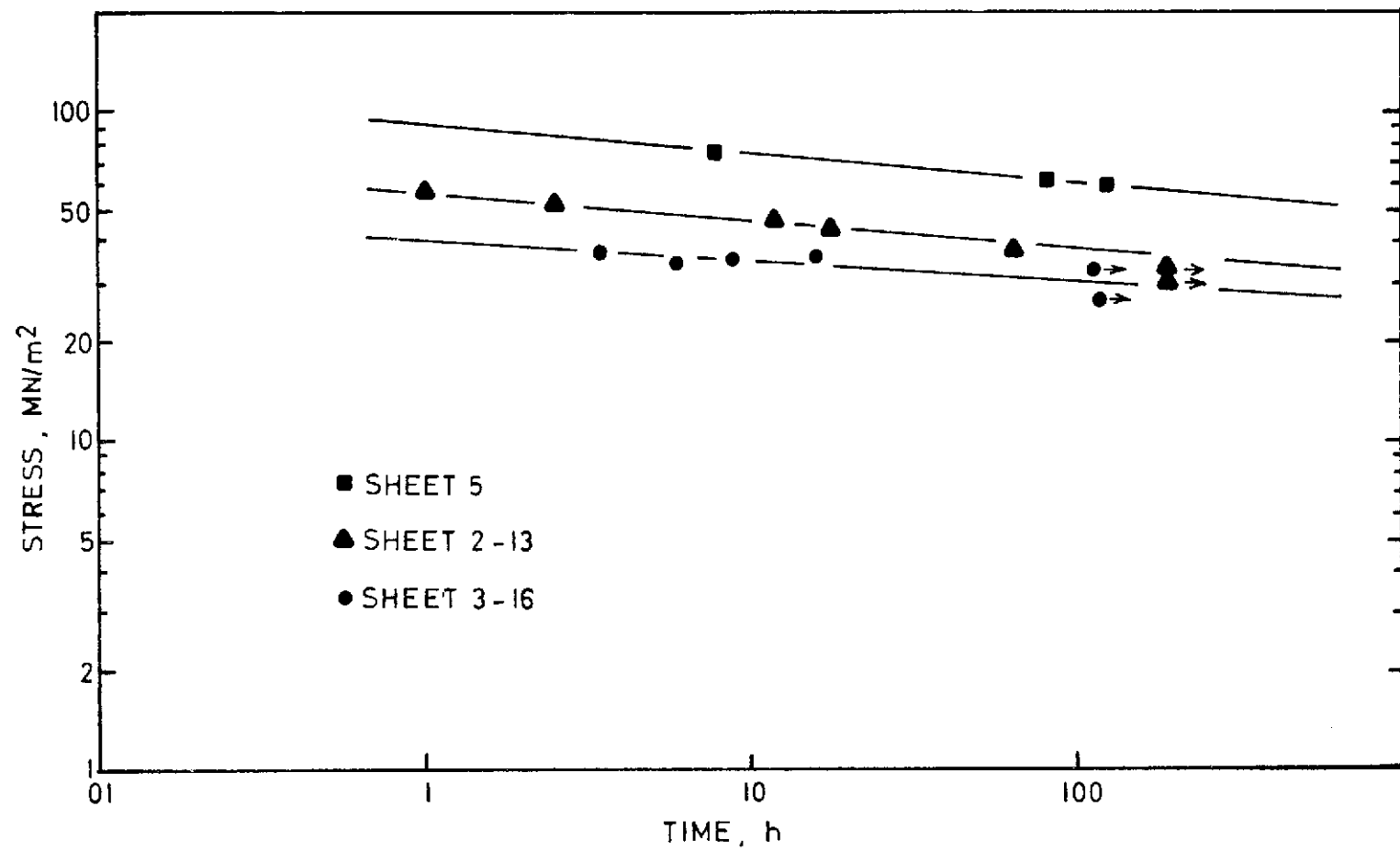
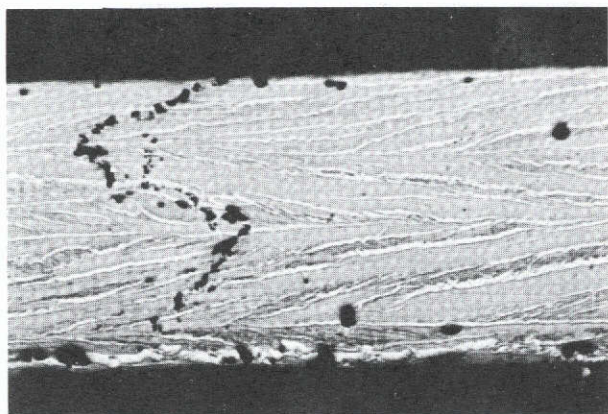
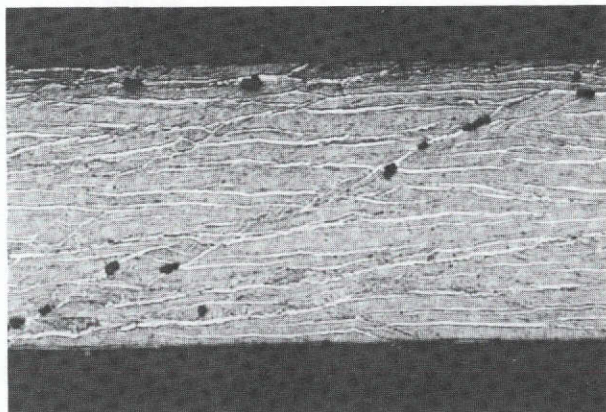


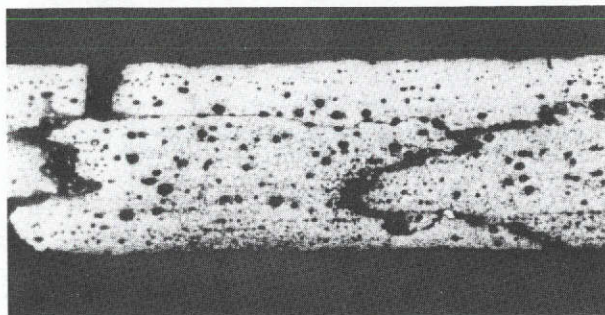
FIGURE 25. 1366 K STRESS RUPTURE PLOTS FOR LONGITUDINAL TEST
SAMPLES OF VARIOUS Ni-Cr-ThO₂ ALLOYS



a) Sheet 3-18 Longitudinal
122 h at 27.6 MN/m²
failed on unloading



b) Sheet 2-13 Longitudinal
190 h at 34.5 MN/m²
no failure



c) TD NiCr Longitudinal
330 h at 41.6 MN/m²
failed on unloading

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FIGURE 26. MICROSTRUCTURES OF Ni-Cr-ThO₂ ALLOYS FOLLOWING STRESS RUPTURE TESTING AT 1366 K (x100)
ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

3. Task III: Development of a Ni-Cr-Al-ThO₂ Alloy

The purpose of this task was to use a modified pack deposition process to produce an oxidation resistant Ni-Cr-Al-ThO₂ alloy with mechanical properties equivalent to the best Ni-Cr-ThO₂ alloy produced in Task II (i.e. Sheet 2-13). The target minimum properties for the alloy are given in Appendix B.

The approach used was to conduct laboratory experiments involving the simultaneous deposition of chromium and aluminum and subsequent diffusion into the Ni-ThO₂ sheet. Two alloy compositions, Ni-16Cr-3.5Al-2ThO₂ and Ni-16Cr-5Al-2ThO₂, were to be produced and evaluated for oxidation resistance and mechanical properties. Process scale-up, to produce sheets 610 x 1220 mm, was to be conducted on the better of the two compositions.

3.1 Material Procurement

The laboratory studies were conducted using TD Ni Heat 3120 (used in Task I) and three sheets 635 x 1270 mm of TD Ni Heat 3216 were obtained for the process scale-up portion of this task. The certified mechanical properties and chemical composition of Heat 3216 are shown in Tables XXII and XXIII. Those of Heat 3120 were given previously in Tables I and II (Section 1.1).

TABLE XXII. TRANSVERSE MECHANICAL PROPERTIES OF Ni-ThO₂ (TD Ni HEAT 3216) USED IN TASK III PROCESS SCALE-UP

Property								
Room Temperature					1366 K			
Gauge mm	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	105° Bend Test	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	Stress Rupture h @ 38MN/m ²
0.25	320	435	10.5	1t	103	104	2	>20

TABLE XXIII. CHEMICAL COMPOSITION OF Ni-ThO₂ USED IN TASK III PROCESS SCALE-UP

Ni-ThO ₂ Heat	Composition in Weight Percentage							
	Co	Cu	Fe	Cr	S	C	ThO ₂	Ni
3216	0.023	0.0021	0.0027	0.0012	0.0017	0.0015	2.12	bal.

The aluminum powder used to modify the basic chromizing pack was SA-23 grade from Alcan. Heat treatment of the blended powder is described in the following sections.

3.2 Preliminary Laboratory Studies

Scouting-type experiments were conducted on the possibility of producing the Ni-Cr-Al-ThO₂ alloy using a duplex diffusion process. These experiments employed a pack containing 10Al/85Cr/5ThO₂ (heat treated 2 h at 920 K) and small Ni-ThO₂ samples (0.32 x 25 x 102 mm). Processing conditions were two 16 h deposition cycles at 1477 K followed by 48 h at 1477 K to homogenize the samples. Following surface grinding to about 0.25 mm, the samples contained 15% Cr and 4% Al and had longitudinal tensile properties as follows:

UTS at room temperature	900 MN/m ²
at 1366 K	87.5 MN/m ²
ductility at room temperature	18%
at 1366 K	4%
stress rupture at 1366 K	>100 h at 39.6 MN/m ²

These properties suggested that the proposed process was feasible and further work was initiated.

3.2.1 Pack Stability Study

Experiments were conducted to determine the reproducibility of the duplex process using a temperature of 1477 K and times up to 70 h. Powder packs were prepared by heat treating blends of aluminum and the standard chromizing pack material (95% Cr, 5% ThO₂). Table XXIV is a summary of the aluminum and chromium concentrations measured in alloy samples produced with each of the four packs. For a given pack, the highest aluminum concentration was produced in the first samples processed following preparation of the pack. The aluminum deposition dropped rapidly at first but gradually stabilized at values at the low end of the aluminum compositional range.

TABLE XXIV. SUMMARY OF DUPLEX DEPOSITION DATA (1477 K)

Aluminum Concentration in Pack wt. %	Number of Samples Examined	Range of Alloy Compositions Measured	
		Aluminum wt. %	Chromium wt. %
3.3	2	1.0 - 1.5	16 - 17
5	8	3.0 - 4.1	14 - 19
8	10	3.8 - 5.3	14 - 19
10	4	5.2 - 7.0	10 - 17

As described previously, the duplex packs had been prepared by blending aluminum powder with the standard chromizing pack and heat treating at 920 K to promote alloying. Following this treatment, x-ray studies showed that no free aluminum remained in the pack. However, subsequent studies showed that even after 16 h at 1477 K there was a considerable amount of a chromium-aluminum intermetallic (possibly Cr_2Al) left in the pack. This intermetallic phase disappeared after an additional 24 h at 1477 K leaving a solid solution of aluminum in the chromium lattice. It was concluded then that the initially high aluminum deposition rate was associated with the higher activity of aluminum in the intermetallic phase. In actual service, the packs also appeared to undergo a continued slow reduction in aluminum deposition rate and it was thought that this was caused by the gradual depletion of aluminum due to oxidation and to alloying with the Ni-ThO₂ sheets being processed.

3.2.2 Effect of Temperature on Deposition Rates

A series of experiments was conducted to determine the effect of temperature on the absolute as well as relative deposition rates of aluminum and chromium. Sample coupons of Ni-ThO₂ sheet, nominally 0.3 mm thick, were processed in the 8% Al pack for times up to 48 h at temperatures of 1477, 1505 and 1533 K. The combined aluminum and chromium depositions are shown in Figure 27; Table XXV gives the aluminum and chromium concentrations at various times at 1477 and 1533 K. At both temperatures the deposition ratio of aluminum to chromium decreased with time which suggested that the deposition and diffusion rates for aluminum were more sensitive to compositional effects than were the corresponding rates for chromium. The effect of temperature on the aluminum to chromium deposition ratio was not significant within the precision limits for the measurement of aluminum and chromium compositions.

TABLE XXV. DEPOSITION RATES OF ALUMINUM AND CHROMIUM AT 1477 K AND 1533 K

Temperature K	Time h	Concentration (weight percent)		Ratio Al/Cr
		Cr	Al	
1477	16	11.0 ^a	2.2	0.2
	32	16.5 ^a	2.6	0.157
	48	20.0	3.0	0.15
1533	16	17.8	3.0	0.169
	32	23-25	3.6	0.15

a. Determined by subtracting the aluminum concentration from total weight gain.

3.3 Screening Programme

The objective of the screening programme was the selection of the alloy which possessed the optimum combination of oxidation resistance and mechanical properties - formability in particular. The nominal alloy target

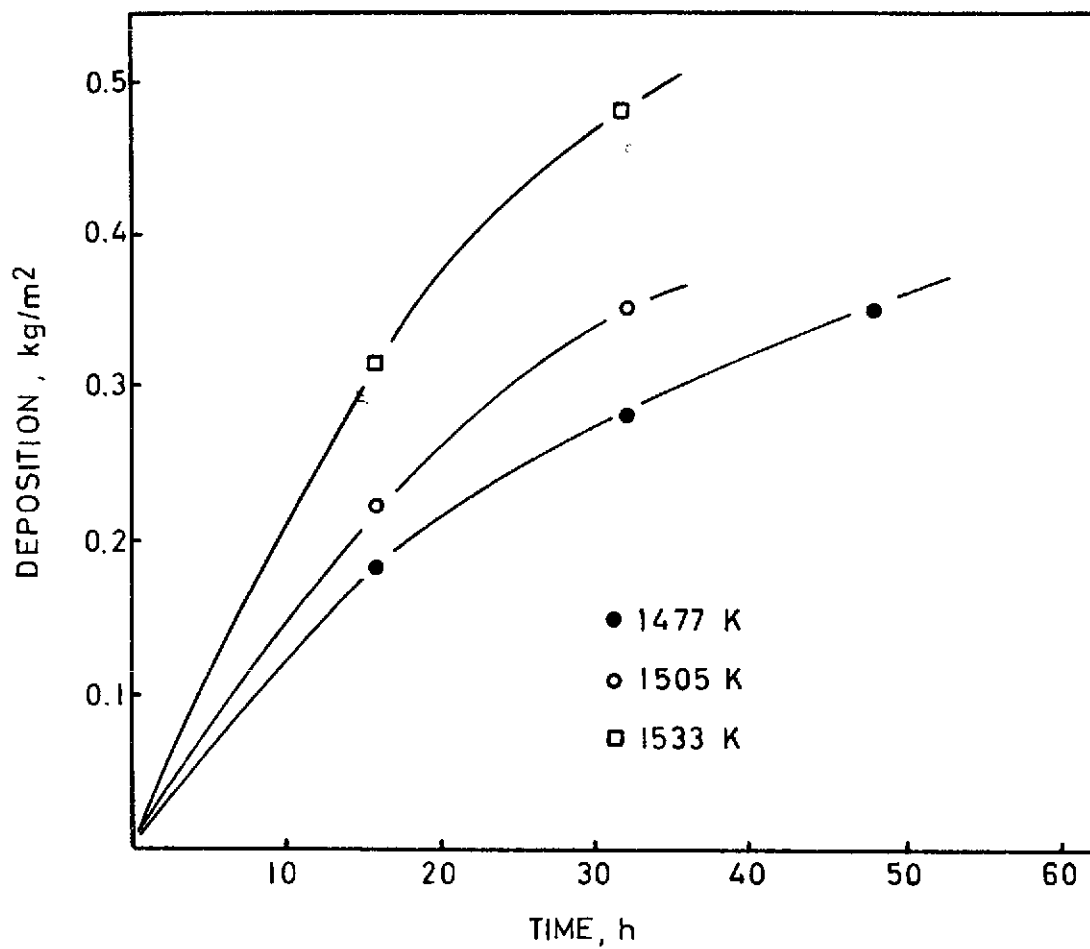


FIGURE 27. EFFECT OF TEMPERATURE AND TIME ON COMBINED ALUMINUM AND CHROMIUM DEPOSITION USING 8% ALUMINUM PACK

compositions were Ni-16Cr-3.5Al-2ThO₂ and Ni-16Cr-5.0Al-2ThO₂ and the nominal thickness of the material was 0.25 mm. After preparation of the alloy samples, the following test programme was initiated:

- (a) Bend properties as a function of heat treated condition.
- (b) Tensile properties at room temperature and 1366 K.
- (c) Stress rupture life at 1366 K and 34.5 MN/m².
- (d) Dynamic oxidation resistance.

3.3.1 Alloy Preparation

The alloys used in the test programme, together with their processing history, are shown in Table XXVI. All samples were prepared by pack treatments at 1477 K, annealed for at least 48 h at 1533 K to effect homogenization and surface ground to 0.25 to 0.30 mm. Alloy 5-6 was produced using a 5% Al pack which had been regenerated by the addition of 3% Al followed by a low temperature alloying treatment. Further regeneration produced alloy 13-14 with the excessively high aluminum content (~10%) and the regeneration technique was therefore modified to a 1% Al addition. Using this procedure, alloys 17-18 and 19-20 were subsequently produced with aluminum concentrations between 4 and 5%.

TABLE XXVI. SUMMARY OF COMPOSITIONS OF ALLOYS USED IN THE SCREENING PROGRAMME

Alloy Number	Processing Conditions		Composition	
	Pack ^a	Time h	Al wt. %	Cr wt. %
3-4	8 Al	53-60	4.2±0.3	17±1
7-8	*	51	3.7±0.3	15±1
11-12	*	52-55	2.9±0.2	16.9±1
1-2	5 Al	60-70	3.9±0.3	17±1
5-6	* + 3%	57	5.5±0.4	17.5±1
9-10	*	62	3.4±0.3	18.2±1
13-14	* + 3%	60	10±1	14±1
15-16	*	64	4.2±0.3	15.2±1
17-18	* + 1%	65	4.0±0.3	16.1±1
19-20	* + 1%	64	4.6±0.3	16.8±1

- a. Alloys are tabulated in chronological order of processing. A "*" signifies that no fresh aluminum was added to the pack following processing of the previous alloy. A "* + 1%" signifies that 1% Al was added to the pack used to process the previous alloy.

3.3.2 Bend Characteristics

Because of the possibility of the formation of the γ' intermetallic phase (Ni_3Al) in Ni-Cr-Al alloys containing greater than about 4% Al, the bend properties of the alloys were measured following a variety of heat treatments. Samples were annealed in hydrogen at 1477 K for 2 h and were then given one of the following treatments:

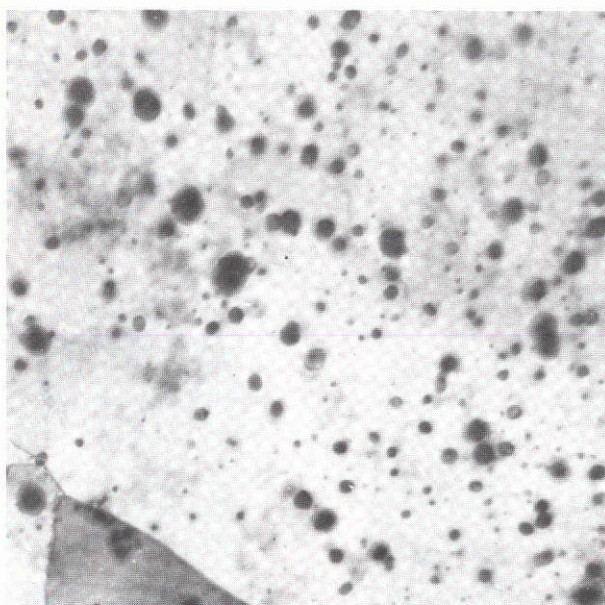
- water quenched
- normally cooled in hydrogen
- water quenched and aged for 16 h at 978 K
- normally cooled and aged for 16 h at 978 K

Thin foils were made from these bend test samples and were examined by transmission electron microscopy. Identification of the γ' phase was made by direct observation of the precipitate in the foil and was confirmed by the existence of the (100) and (110) superlattice points in selected area electron diffraction patterns (Figures 28 through 30). The results of this study are given in Table XXVII and show that γ' was formed in all of the alloy samples during the aging treatment. The normal cooling provided a sufficiently high cooling rate to suppress precipitation in the 3.9% Al alloy but not in the 5.5% Al alloy. It was apparent that the presence of the γ' phase did not impair the bend properties of any of the alloys investigated. The poor bend ductility of the 4.2% Al alloy was traced to surface porosity which had not been removed during the grinding operation. It was likely that a combination of these stress raisers in the surface of the material and the presence of a γ' phase contributed respectively, to the initiation and propagation of cracks through the sample.

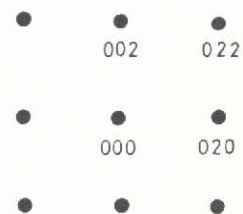
TABLE XXVII. SUMMARY OF THIN FOIL γ' DETECTION STUDY

Alloy Number	Aluminum Concentration wt. %	Heat Treated Condition	γ' Detected	Minimum Radius for 105° Bend
1-2	3.9	Normally Cooled	No	1t
		Water Quenched	No	1t
		Water Quenched and Aged	Yes	1t
3-4	4.2	Normally Cooled	n.d. ^a	>3t
		Water Quenched	n.d. ^a	1t
		Water Quenched and Aged	Yes	3t
5-6	5.5	Normally Cooled	Yes	1.5t
		Water Quenched	No	1.5t
		Water Quenched and Aged	Yes	n.d.

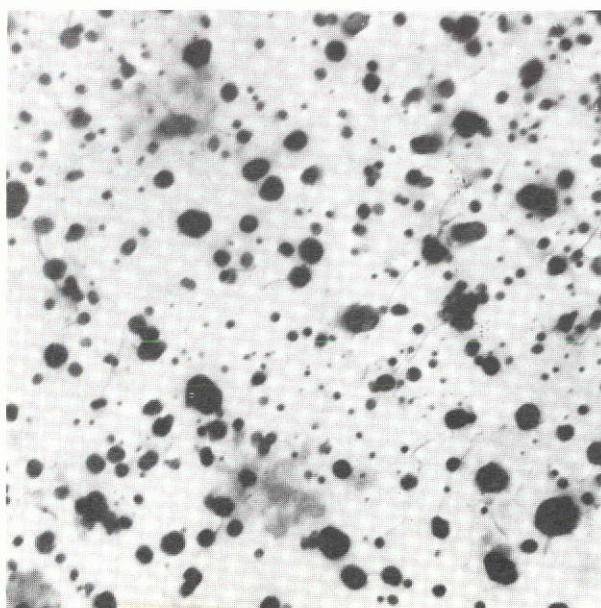
a. Not determined: insufficient material available.



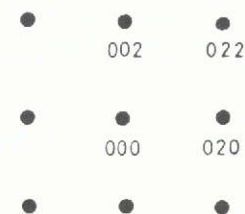
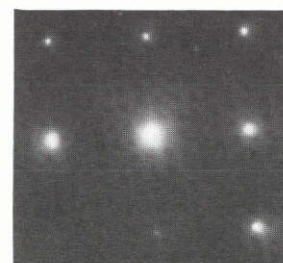
a) Alloy 1-2: 3.9% Al



(100) ZONE AXIS

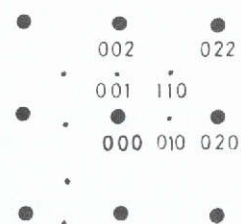
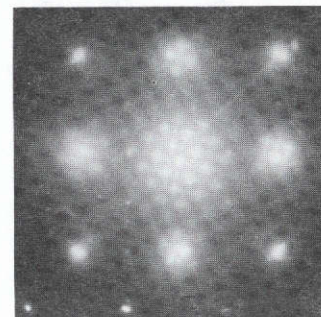
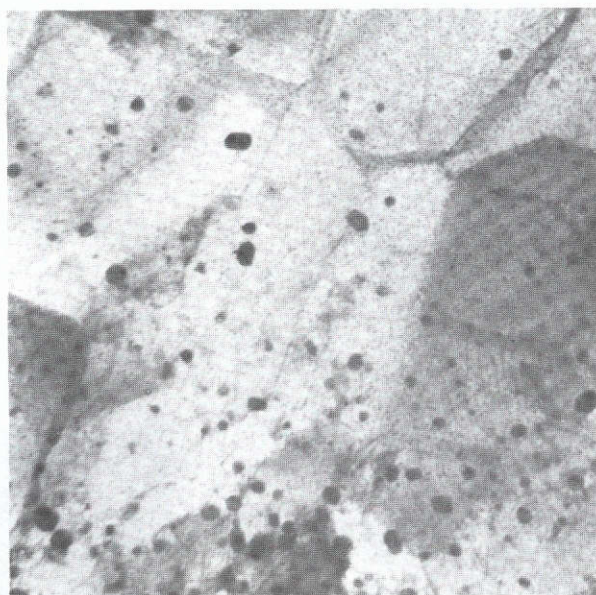


b) Alloy 5-6: 5.5% Al



(100) ZONE AXIS

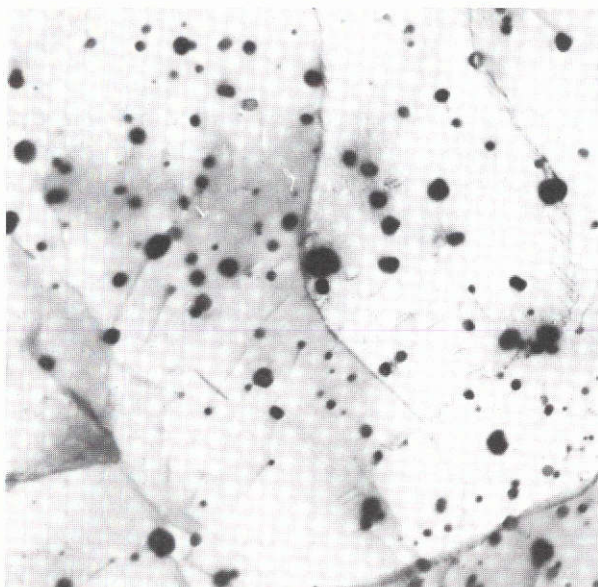
FIGURE 28. TRANSMISSION ELECTRON MICROGRAPHS AND SELECTED AREA ELECTRON DIFFRACTION PATTERNS FOR WATER QUENCHED Ni-Cr-Al-ThO₂ ALLOY (x20,000)



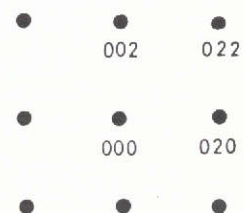
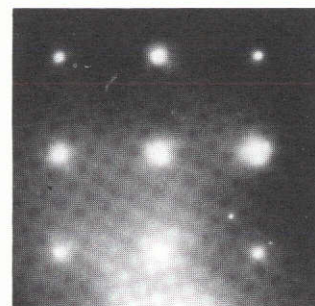
(100) ZONE AXIS

FIGURE 29. TRANSMISSION ELECTRON MICROGRAPHS AND SELECTED AREA ELECTRON DIFFRACTION PATTERNS FOR QUENCHED AND AGED Ni-Cr-Al-ThO₂ ALLOY 1-2 CONTAINING 3.9% Al (x20,000)

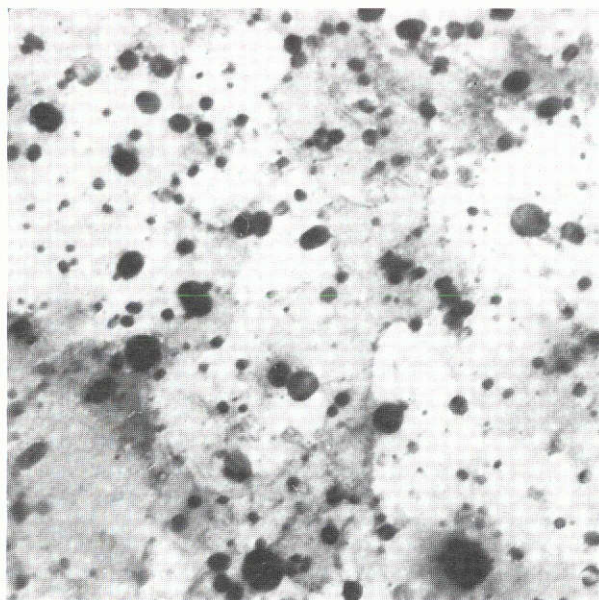
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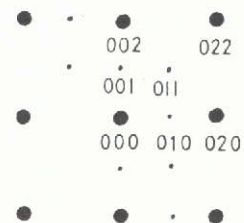
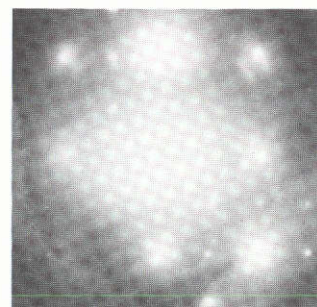
a) Alloy 1-2: 3.9% Al



(100) ZONE AXIS



b) Alloy 5-6: 5.5% Al



(100) ZONE AXIS

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FIGURE 30. TRANSMISSION ELECTRON MICROGRAPHS AND SELECTED AREA ELECTRON DIFFRACTION PATTERNS FOR NORMALLY COOLED Ni-Cr-Al-ThO₂ ALLOYS (x20,000)

3.3.3 Mechanical Properties

Tensile and stress rupture testing of all alloys was done on transverse samples in the normally cooled or water quenched heat treated condition. The room temperature tensile data are presented in Figures 31 and 32 and show that:

- (a) In the normally cooled condition the yield and ultimate tensile strengths increased rapidly with increasing aluminum content in the region of 4% Al. The tensile ductility decreased slightly.
- (b) In the water quenched condition the yield and ultimate strengths also increased but in the compositional range 4.6 to 5.5% Al. The tensile ductility, however, remained relatively high (>15%).

The tensile properties for the alloys at 1366 K were independent of composition and heat treatment within the precision of the measurements and are given in Table XXVIII.

TABLE XXVIII. TENSILE PROPERTIES^a AT 1366 K

Alloy	% Al	Condition	0.2% YS MN/m ²	UTS MN/m ²	Elongation % in 25.4 mm
TD Ni Heat 3120	0	As-received	95	101	3
9-10	3.4	Water Quenched	95	98	4
7-8	3.7	Water Quenched	90	93	5
1-2	3.9	Normally Cooled	91	97	3
3-4	4.2	Normally Cooled	84	90	5
5-6	5.5	Water Quenched	92	95	5

a. Strain rate was $8.3 \times 10^{-4} \text{ s}^{-1}$ to failure.

Transverse samples of nominally Ni-16Cr-2ThO₂ alloys containing 3.9, 4.2 and 5.5% Al were stress rupture tested at 1366 K and a stress level of 34.5 MN/m². Times for all samples exceeded 100 h and elongations at failure were about 1% in 25.4 mm. The fact that high elongations were not observed lent further support to the theory that some microstructures were more susceptible to the creep degradation phenomenon.

3.3.4 Dynamic Oxidation Testing

The final screening test included in the programme was cyclic dynamic oxidation at 1477 K. The test involved the exposure of the as-ground alloy samples to a flowing atmosphere from the combustion of JP4 fuel (air to fuel

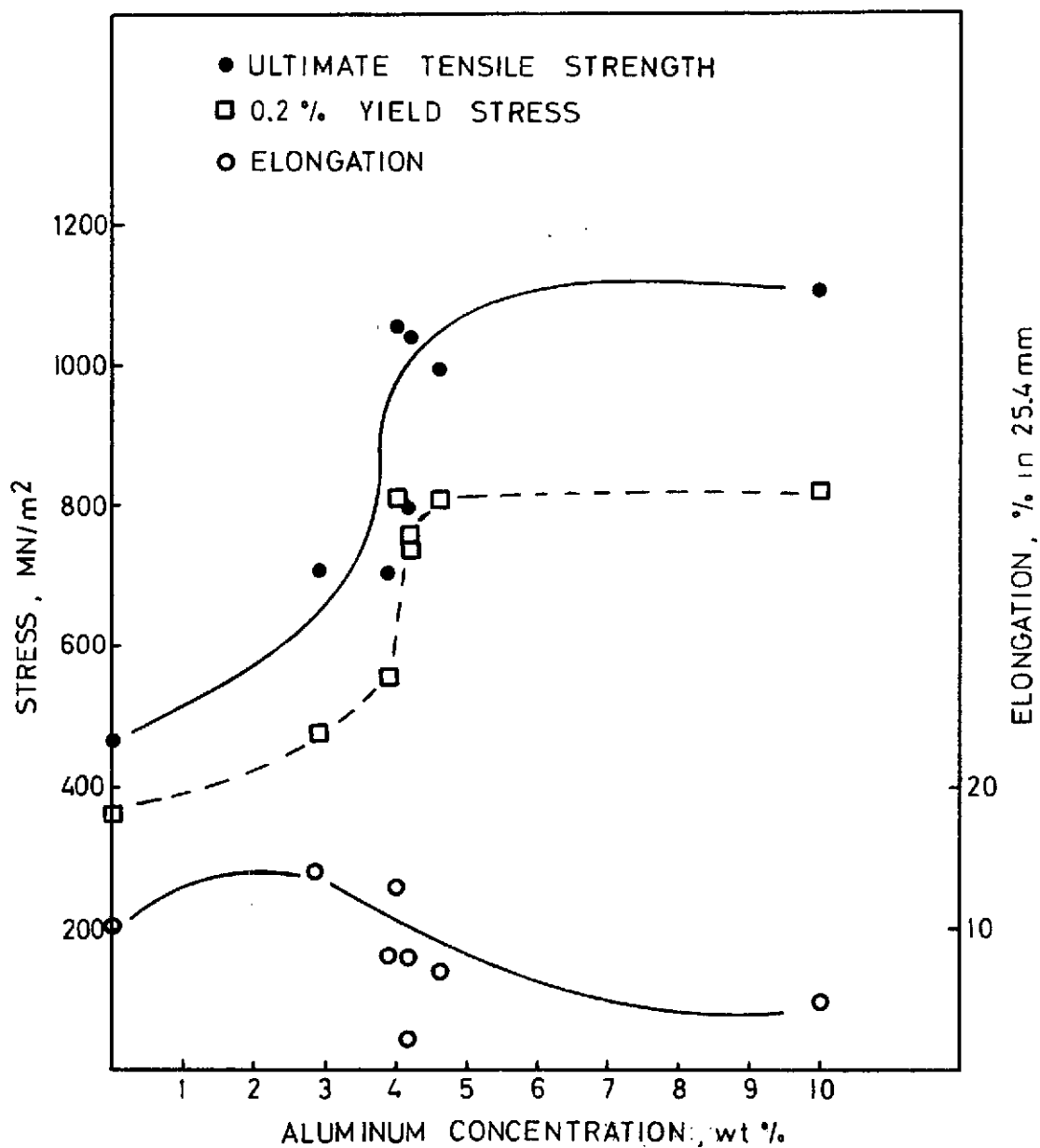


FIGURE 31. ROOM TEMPERATURE TENSILE PROPERTIES OF NORMALLY COOLED ALLOYS AS A FUNCTION OF ALUMINUM CONCENTRATION FOR NOMINALLY Ni-16Cr-Al-2ThO₂ ALLOYS

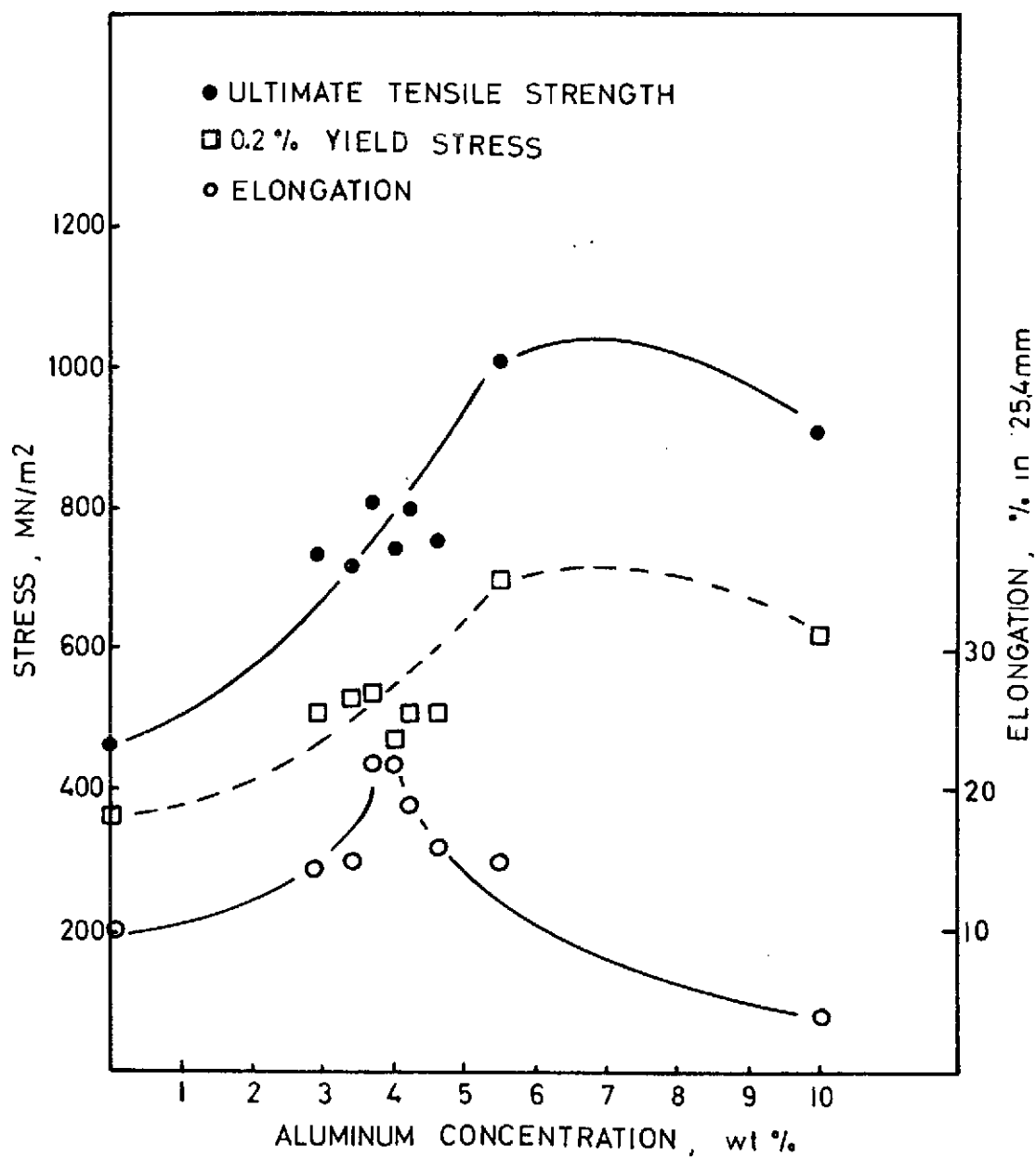


FIGURE 32. ROOM TEMPERATURE TENSILE PROPERTIES OF WATER QUENCHED ALLOYS AS A FUNCTION OF ALUMINUM CONCENTRATION FOR NOMINALLY Ni-16Cr-Al-2ThO₂ ALLOYS

ratio of 15:1 by weight). The gas impinged on a rotating sample bundle with a velocity of about Mach 0.3 from a converging-diverging exit nozzle (Figure 33). The testing programme was 140 cycles of 1200 seconds at temperature and 15 seconds cooling; weight changes of the alloys were determined at the completion of each test. Accuracy of temperature control was about ± 10 K. The results from the tests are shown in Table XXIX. Test 1 was run at slightly higher temperature than Test 2 owing to an unintended temperature overshoot to about 1505 K for about 60 seconds at the start of each hot cycle. The difference in temperature is indicated by the difference in the weight change measurements of the standard Ni-20Cr-2ThO₂ alloy in each test (Sheet 2-13 from Task II). The difference in performance of the aluminum-containing alloys in each test, however, was very small when compared with the substantial improvement of the oxidation resistance of these alloys over the binary alloy.

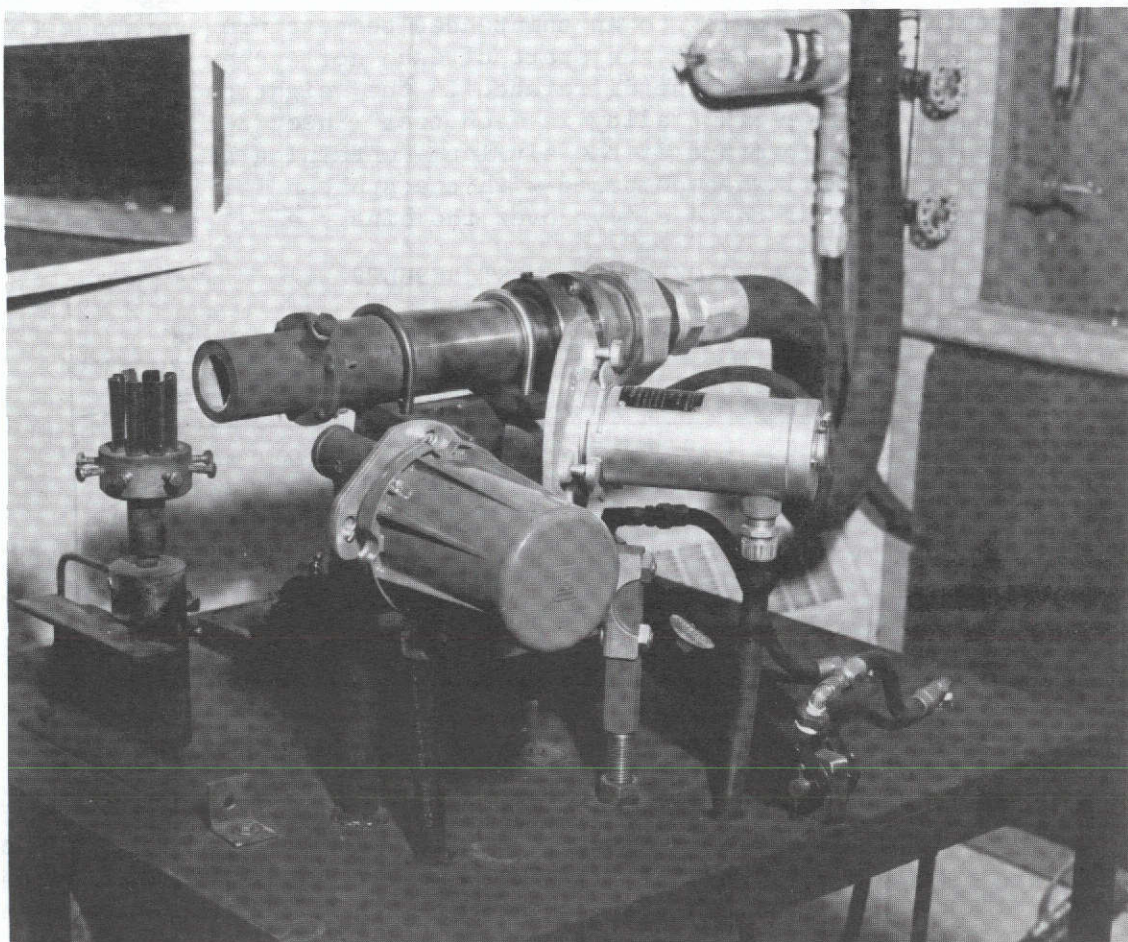
TABLE XXIX. CYCLIC DYNAMIC OXIDATION TEST RESULTS

Test	Alloy	% Al	Weight Change (kg/m ²)	
			Average	Range
1	1-2	3.9	-0.018	-0.01 to -0.022
	3-4	4.2	-0.038	-0.016 to -0.049
	Ni-Cr-ThO ₂ (Sheet 2-13)	0	-0.35	-0.33 to -0.38
2	7-8	3.7	+0.004	+0.003 to +0.005
	5-6	5.5	+0.002	-0.002 to +0.007
	Ni-Cr-ThO ₂ (Sheet 2-13)	0	-0.26	-0.24 to -0.28

All of the aluminum-containing alloys formed a light grey surface oxide consisting predominately of Al₂O₃. There were traces of a green oxide (presumably Cr₂O₃ or NiCr₂O₄) at the very edges of the samples and on the side of the sample not exposed to the flame. Chromium depletion as observed by electron microprobe scans occurred only in the Ni-Cr-ThO₂ alloy and penetrated to the center of the sample (about 0.2 mm). Isolated porosity was observed in all samples but was considered to be insignificant. Figures 34, 35 and 36 show representative areas of samples from Test 2. Both aluminum-modified alloys had regions where the surface oxide had spalled and the Ni-Cr-ThO₂ samples showed severe oxidation and material loss.

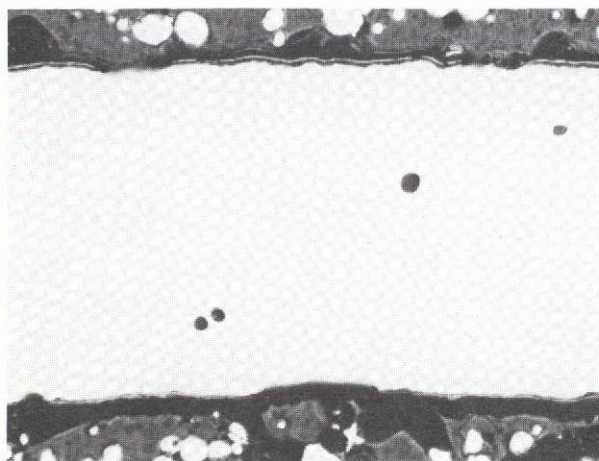
3.4 Alloy Selection

The objective of the screening programme had been to compare the mechanical properties and oxidation resistance of two alloys: Ni-16Cr-3.5Al-2ThO₂ and Ni-16Cr-5Al-2ThO₂. Table XXX is a summary of typical properties for alloys of these two nominal compositions. The tabulated values were obtained by averaging the test results for alloys having aluminum contents within $\pm 0.5\%$ Al of the nominal compositions. It is important to note that for nominal aluminum concentrations of 3.5% the room temperature tensile strengths were relatively insensitive to cooling rates and, although above

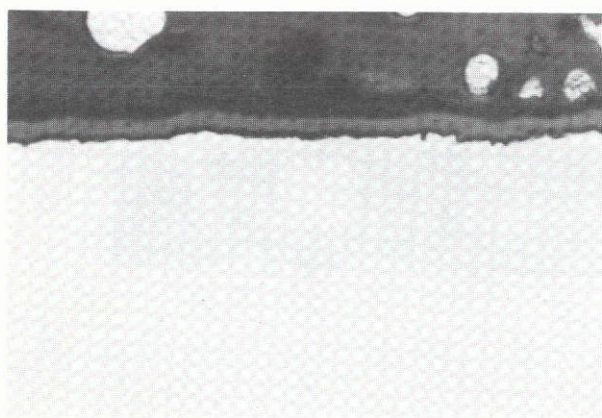


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FIGURE 33. DYNAMIC OXIDATION TEST RIG



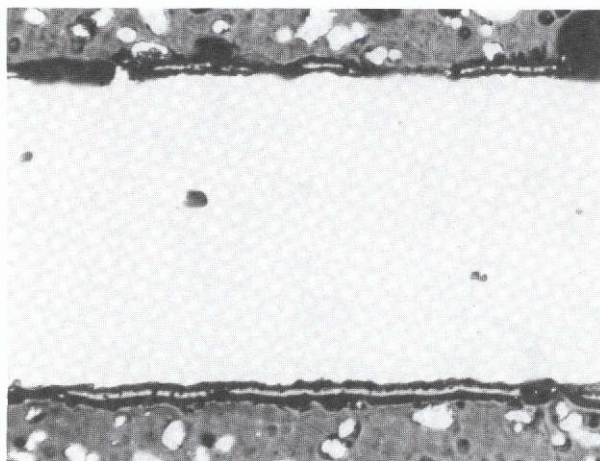
a) Sample Thickness (x150)



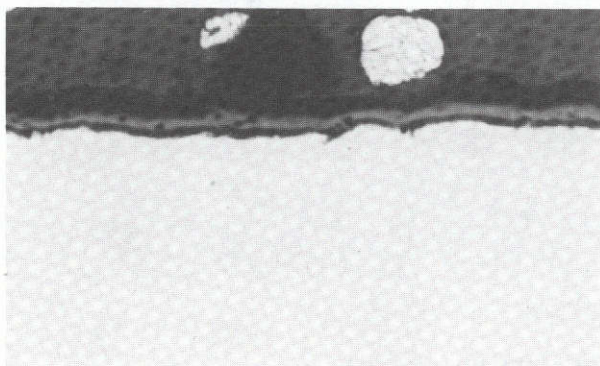
b) Surface Oxide (x400)

FIGURE 34. OXIDATION TEST SAMPLES AFTER EXPOSURE AT 1477 K (TEST 2)
ALLOY 7-8 NOMINALLY Ni-15Cr-3.7Al-2ThO₂, UNETCHED

ALLOY 7-8 NOMINALLY Ni-15Cr-3.7Al-2ThO₂

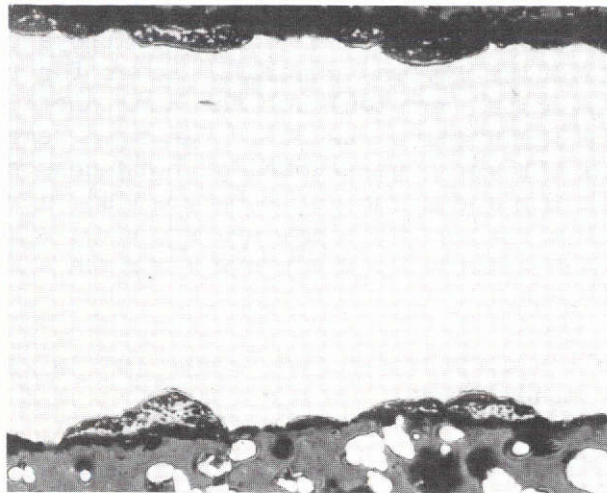


a) Sample Thickness (x150)

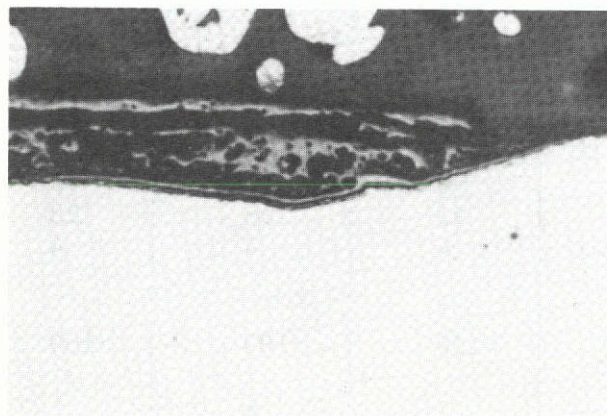


b) Surface Oxide (x400)

FIGURE 35. OXIDATION TEST SAMPLES AFTER EXPOSURE AT 1477 K (TEST 2)
ALLOY 5-6 NOMINALLY Ni-17.5Cr-5.5Al-2ThO₂, UNETCHED

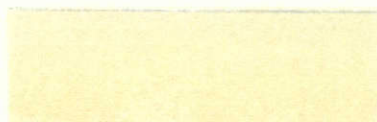


a) Sample Thickness (x150)



b) Surface Oxide (x400)

FIGURE 36. OXIDATION TEST SAMPLES AFTER EXPOSURE AT 1477 K (TEST 2) OF NOMINALLY Ni-20Cr-2ThO₂ SHEET 2-13, UNETCHED



the programme target levels, were lower than those of alloys containing nominally 5% Al. The tensile ductility was generally lower for the 5% Al alloys (particularly the normally cooled version) but the bend ductility was not seriously affected (target bend radius was 3t). Elevated temperature properties were similar for both alloys. Operationally, both compositions could be produced but a water quenching operation would be more difficult in a scaled-up process and with this limitation the final selection of alloy composition was based on a trade-off between room temperature strength and ductility in the normally cooled condition.

The following alloy composition was chosen for the process scale-up portion of Task III and further study:

<u>Component</u>	<u>Level (wt. %)</u>
Cr	16 ± 2
Al	3.5 - 4.0
ThO ₂	2.0 ± 0.4
Ni	Balance

TABLE XXX. TYPICAL PROPERTIES DETERMINED IN SCREENING PROGRAMME

	<u>Ni-16Cr-3.5Al-2ThO₂</u>		<u>Ni-16Cr-5Al-2ThO₂</u>	
	<u>Water Quenched</u>	<u>Normally Cooled</u>	<u>Water Quenched</u>	<u>Normally Cooled</u>
<u>Room Temperature</u>				
0.2% YS, MN/m ²	515	515	620	790
UTS, MN/m ²	725	725	895	1030
Elongation, % in 25.4 mm	17	12	15	7
<u>1366 K</u>				
0.2% YS, MN/m ²	90	90	90	90
UTS, MN/m ²	93	93	93	93
Elongation, % in 25.4 mm	4	4	4	4
Stress to Rupture, h @ 34.5 MN/m ²	>100	>100	>100	>100
Elongation at Failure, % in 25.4 mm	1	1	1	1
<u>Bend Test</u>				
105° on a radius of	1t	1t	1t	2t
<u>Cyclic Dynamic Oxidation Resistance</u>				
Weight change after 50 h at 1477 K, kg/m ²	+0.003	-	+0.003	-

3.5 Process Scale-Up Study

3.5.1 Pack Stability Experiments

Because of the unknown effect of the furnace and cooling zone atmosphere on the oxidation of the aluminum-containing pack, it was arbitrarily decided to start with a pack containing Cr/5ThO₂ blended with 10% Al powder. Following the laboratory procedures to ensure pre-alloying of the constituent powders, the blend was given the following heat treatments:

16 h at 1315 K
64 h at 1477 K

X-ray analyses of powder samples taken after each of the above treatments indicated that the pack was not following the alloying pattern shown by similar packs processed in the laboratory. In fact, Al₂O₃ was detected following the 1477 K heat treatment.

Notwithstanding the formation of Al₂O₃, two furnace cycles of nominally 16 h each at 1533 K were conducted using a sheet of DS Ni (sheet 2-20, 0.25 x 610 x 1070 mm, from the Lot 2 DS Ni used in earlier chromizing studies) and six coupons of TD Ni (Heat 3120, 0.31 x 51 x 51 mm). As an experiment, the bottom side of the sheet was slurry-coated in each cycle using polyvinyl alcohol as a binder.

The appearance of the sheet following this treatment was unlike previous aluminum-containing alloys in that it was more like the standard Ni-Cr-ThO₂ alloy. Bend characteristics and the degree of brittleness during shearing were also indications that the aluminum content was very low. Electron microprobe scans for aluminum confirmed these observations - the alloy contained only about 0.5% Al. On the positive side, however, the slurry coating was very effective in minimizing the sheet surface area having little or no deposition. In fact, the technique was so effective that it was recommended for use in all further scale-up studies.

X-ray analysis of the powder after the first 16 h cycle confirmed the existence of considerable amounts of Al₂O₃ and subsequent chemical analyses of pack samples taken at various stages of the processing showed that the oxygen content of the pack had been relatively constant and equal to the level in the original powder blend (about 7% oxygen). The oxygen originally present would have been there primarily as Cr₂O₃ and the addition of aluminum powder plus the extended pretreatments resulted in the reduction of Cr₂O₃ and the simultaneous oxidation of aluminum to Al₂O₃. This amount of oxidation effectively eliminated the aluminum activity in the pack and therefore accounted for the very low aluminum concentration in the alloy sheet. The oxidation of the pack was gradual, however, and it was decided to blend aluminum powder with the oxidized Cr/10Al/5ThO₂ pack and process a second slurry-coated DS Ni Sheet (2-21) and additional TD Ni coupons. Approximately 2.5% Al was added to a portion of the pack and a furnace cycle of 16 h at 1533 K resulted in the following depositions:

	<u>%</u>	<u>Total Cr plus Al</u> <u>kg/m²</u>
Sheet 2-21	14.8	0.194
Coupons	15.2 ± 0.6	0.211 ± 0.009

This increase in the deposition rate was attributed to the presence of aluminum and, indeed, electron microprobe scans showed that the alloy contained about 2.5% Al and 12% Cr. This result was encouraging and small pack experiments were conducted in the large furnace to define the required aluminum enrichment required to give 3.5 to 4.0% Al and nominally 16% Cr. Aluminum powder was blended with portions of the oxidized Cr/10Al/5ThO₂ powder to make three small packs containing 1, 3 and 5% free aluminum. Coupons of TD Ni were given two furnace cycles of 16 h at 1533 K in each of these packs and the deposition results and electron microprobe estimates of composition are given in Table XXXI.

TABLE XXXI. SUMMARY OF SMALL SCALE EXPERIMENTS TO
DEPOSIT CHROMIUM AND ALUMINUM SIMULTANEOUSLY

Pack	16 h at 1533 K				32 h at 1533 K			
	Total Deposition		Microprobe		Total Deposition		Microprobe	
	%	kg/m ²	% Al	% Cr	%	kg/m ²	% Al	% Cr
1% Al	15.5	0.223	2.2	14	23.1	0.368	2.6	21
3% Al	15.4	0.223	3.2	14	22.3	0.352	3.1	19
5% Al	17.5	0.261	4.3	13	24.1	0.390	4.4	18

The chromium concentrations were only approximate (±2%) because measurements were obtained from unhomogenized samples which had large surface-to-center chromium concentration gradients. The aluminum concentrations were relatively uniform through the strip thickness and the tabulated values are therefore more accurate.

Based on the above results, it was concluded that an alloy containing 3.5 to 4.0% Al and nominally 16% Cr could be produced using the existing oxidized Cr/10Al/5ThO₂ pack blended with about 4% Al powder.

3.5.2 Processing of Large Sheets

A pack containing 4.2% Al blended with the oxidized Cr/10Al/5ThO₂ powder was prepared and two TD Ni sheets (Lot 3216; 0.28 x 635 x 1270 mm) were processed at 1533 K using the slurry coating procedure for the lower sheet surfaces. Samples were taken after a 20 h cycle and electron microprobe

analysis showed an abnormally high aluminum content. To compensate for the high aluminum content, the second cycle of 6 h at 1533 K was conducted using a pack containing no aluminum (i.e. Cr/5ThO₂). The results from these runs were as follows:

TABLE XXXII. PROCESSING DATA FOR SCALED UP DUPLEX PROCESS

Sheet	Heat Treatment at 1533 K				Microprobe Data	
	20 h		26 h		20 h	
	% (Cr+Al)	kg/m ²	% (Cr+Al)	kg/m ²	% Cr	% Al
4-1	18.9	0.303	20.9	0.343	12	6
4-2	17.9	0.293	20.1	0.335	12	6

The reason for the unexpectedly high aluminum deposition was believed to have been the residual aluminum activity in the oxidized Cr/10Al/5ThO₂ pack which resulted from the inadvertent inclusion of a portion of the pack which had been enriched with 2.5% Al for the trial processing of Sheet 2-21. It was very clear that control of the alloy composition was considerably more difficult in the scaled-up duplex process than in the laboratory process.

The two sheets were subsequently annealed for 68 h at 1505 K to effect homogenization. Areas on each sheet suffered from the peeling phenomenon that was observed in the preliminary studies and which was subsequently related to an aluminum concentration of greater than about 6% in the alloy. Samples of the peeled coating were identified as Ni₃Al.

3.5.3 Stretcher Leveling

Stretcher leveling of sheets 4-1 and 4-2 was done at the Cyril Bath Co. in Cleveland, Ohio, as had been established for the Standard Practice for processing of Ni-Cr-ThO₂ alloy sheets (Section 2.5). Considerable difficulty was experienced during the leveling operation: the as-annealed sheets could not be stretched more than about 3 mm before fracture occurred. The edges of each piece were then polished to remove any stress raisers and were stretched to adequate flatness with permanent elongations of 13 to 19 mm. This high degree of notch sensitivity may be inherent in the Ni-Cr-Al-ThO₂ system but it may be common only to alloys containing greater than about 4% Al. In order to minimize the possibility of sheet breakage, however, it was recommended that sheet stock should have all edges smoothed prior to stretcher leveling.

3.5.4 Surface Grinding

Surface grinding was done at the Hill Acme Co. in Cleveland, Ohio, as had been established for the Ni-Cr-ThO₂ Standard Practice. Difficulties were also encountered in this operation: the peeled surface layers precluded the use of the established taping technique for sheet hold-down and forced grinding with a mechanical clamping procedure until integrity of the surface layer was achieved. The normal taping procedure was then used for the remainder of the grinding operation. Approximately 0.076 mm was ground from each side of the sheets but the belt wear was very severe and was attributed to the presence of the hard intermetallic surface layer. Gauge control was not so good as expected and it was believed that non-uniformity in the starting stock caused by localized peeling was the prime contributing factor.

3.6 Evaluation of Material Produced in Process Scale-Up

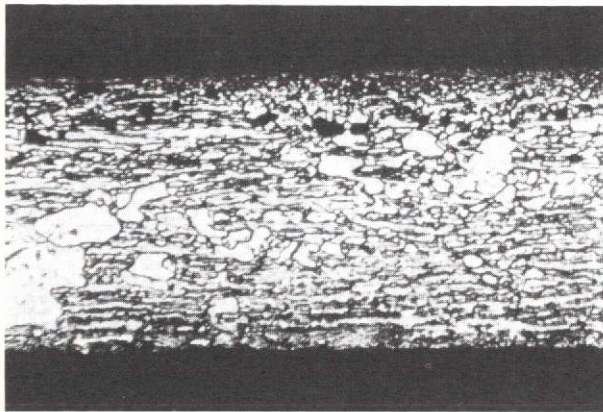
Wet chemical analysis of samples taken from several areas of Sheets 4-1 and 4-2 gave the following results for average aluminum and chromium concentrations:

TABLE XXXIII. CHEMICAL COMPOSITION OF SHEETS 4-1 AND 4-2

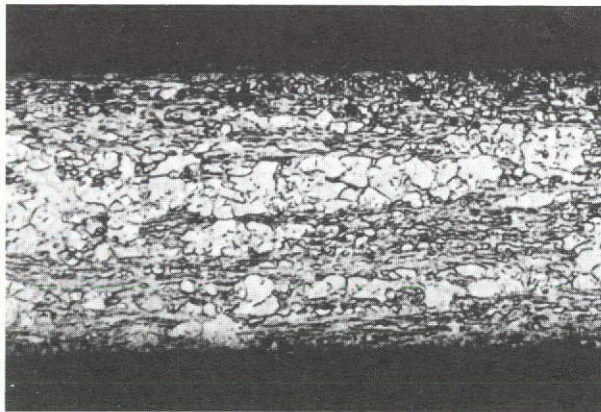
Sheet	Composition (wt. %)	
	Al	Cr
4-1	6.8	12.5
4-2	6.3	13.4

These data supported the in-process microprobe study which showed that the aluminum concentration had exceeded the target of 4%. There was also evidence at this time that the aluminum concentration was as low as 4.7% in some areas in Sheet 4-2.

Samples were taken from various positions of the two sheets and subjected to a test programme which included metallographic analysis, bend testing, room and elevated temperature tensile testing and evaluation of stress rupture life. A typical grain structure is shown in Figure 37 and a summary of the mechanical property data is given in Table XXXIV.



a) Longitudinal Cross Section



b) Transverse Cross Section

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FIGURE 37. MICROSTRUCTURE OF Ni-Cr-Al-ThO₂ SHEET 4-1 (x150)
ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

TABLE XXXIV. TRANSVERSE MECHANICAL PROPERTIES OF Ni-Cr-Al-ThO₂ SHEETS PRODUCED IN TASK III

Property	Sheet 4-1	Sheet 4-2
<u>Room Temperature</u>		
0.2% YS, MN/m ²	840	765
UTS, MN/m ²	1235	1100
Elongation, % in 25.4 mm	8	8
<u>1366 K</u>		
0.2% YS, MN/m ²	70	68
UTS, MN/m ²	72	72
Elongation, % in 25.4 mm	7	7
<u>Stress Rupture</u>		
Failed at 27.6 MN/m ²	>120 h	not tested
34.5 MN/m ²	37.7 h	14.9 h
41.4 MN/m ²	1.9 h	not tested
Elongation, % in 25.4 mm	5 to 60	about 50
<u>Bend Test</u>		
105° on radius of		
Longitudinal	1.5t	1.5t
Transverse	3t	1.5t

The reason for the appearance of the mixed grain structure shown in Figure 37 and the associated low strength at 1366 K is not completely clear. The presence of equiaxed grains would be expected to decrease the high temperature strength in accordance with the grain aspect ratio relationship suggested by Wilcox and Clauer (ref. 6) and indeed some equiaxed grains were also observed in sheet from TD Ni Heat 3216 (used to produce sheets 4-1 and 4-2). In addition, the certified 1366 K ultimate tensile strength of this heat (Table XXII) was the lowest of the three batches of TD Ni that had been used in the programme to date (Heat 3120 and 3293 had certified 1366 K UTS values of 118 and 124 MN/m² respectively). It therefore seems that the optimum TD Ni structure for chromizing and aluminizing must possess a minimum of equiaxed grains and a maximum of grain boundaries oriented parallel to the sheet plane such that the certified ultimate tensile strength at 1366 K is a minimum of 105 to 110 MN/m². (Note that these are "certified" values; testing at Sherritt Gordon showed the strengths of Heats 3120 and 3293 to be lower than the certified values. A comparable minimum strength level, when tested at Sherritt, would be about 95 MN/m².)

3.7 Task Completion

Portions of Sheets 4-1 and 4-2 were forwarded to the NASA Project Manager to complete the Task III material requirements. The physical dimensions of the sheets were as follows:

<u>Sheet</u>	<u>Size (mm)</u>	<u>Weight (kg)</u>	<u>Gauge Range (mm)</u>
4-1A	406 x 508	0.41	0.214 to 0.264
4-2A	432 x 610	0.57	0.228 to 0.305

The gauge range was established using micrometer measurements at about 102 mm intervals along the sheet edges. The surface finish on the sheets varied from 280 to 510 nm RMS. Metallographic inspection revealed the presence of isolated areas of surface porosity not removed in the grinding operation.

Even though considerable difficulties were encountered in processing the aluminum-modified alloy, further characterization seemed warranted. Thus the following alloy composition was selected for further study:

<u>Component</u>	<u>Composition (wt. %)</u>
ThO ₂	2.0 ± 0.4
Al	4.5 ± 1
Cr	16.0 ± 2
Ni	Balance

4. Task IV Material Characterization

The original objective of this task was to produce either a Ni-Cr-Al-ThO₂ or a Ni-Cr-ThO₂ alloy by a Standard Process and conduct an extensive programme to characterize the mechanical properties and oxidation resistance of the selected alloy. However, because of the non-reproducibility of the duplex process (demonstrated at the end of Task III) and the termination of TD Ni sheet production by Fansteel, the production of several Ni-Cr-ThO₂ sheets from Lot 3 DS Ni was included as contingency. In addition, further study of the duplex process was conducted prior to committal of the only TD Ni sheet available.

4.1 Material Procurement

Fifteen TD Ni 0.25 x 635 x 1270 mm sheets were received, along with several part sheets. Table XXXV summarizes the certification data for the shipment.

TABLE XXXV. MECHANICAL PROPERTIES AND CHEMICAL COMPOSITION
OF TD NI USED IN TASK IV

Heat	Mechanical Properties							
	Room Temperature				1366 K			
	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	105° Bend Test	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	Stress Rupture h at 38 MN/m ²
3852	312	450	12.5	1t	103	126	3.5	>20
3213	366	473	13.5	1t	95	101	4.0	>20
Chemical Composition (wt. %)								
Heat	Co	Cu	Fe	Cr	S	C	ThO ₂	Ni
3852	0.02	0.0011	0.0057	0.001	0.0011	0.003	2.14	bal.
3213	0.024	0.0025	0.002	0.0015	0.0015	0.001	2.11	bal.

Because of the low strength of Heat 3213 sheets (2 full size sheets) these were not used in the production of the aluminum-modified alloy.

4.2 Preliminary Pack Studies

Preliminary studies were conducted in the large furnace using combinations of Cr/Al/ThO₂ and Cr/ThO₂ packs with varied additions of aluminum powder. The objective, as in previous studies, was to provide a pack chemistry suitable for use in the large furnace system and production of sheets with a consistent aluminum concentration.

Three basic packs were prepared:

- A. Cr/Al/ThO₂ (from the existing powder supply used to produce sheets 4-1 and 4-2).
- B. 20% (Cr/ThO₂) and 80% (Cr/Al/ThO₂) heat treated 8 h at 1311 K.
- C. 50% (Cr/ThO₂) and 50% (Cr/Al/ThO₂).

These basic packs were modified with various aluminum additions and used to process coupons of 0.25 mm thick TD Ni (Heat 3120). Following a furnace cycle of 16 h at 1533 K samples were taken for electron microprobe studies. The results from this study are presented in Figure 38. The solid lines show the aluminum deposition for packs modified by the indicated aluminum addition, e.g. Pack B with 2 or 4% Al produced coupons containing 1 or 3% Al respectively. The dotted lines show the aluminum deposition for packs with further aluminum additions, e.g. Pack B with 2% Al followed by a further addition of 3% Al (for a total of 5%) gave 3.5% Al in the coupon. The dotted lines, therefore, indicate continued use of a pack enriched with aluminum for each new sample.

Pack B was selected for further work because it had virtually no aluminum activity (i.e. 0.2% Al deposited) and showed a predictable response when aluminum was added. The data for Pack B were extrapolated to give a value of about 5% Al for the initial aluminum addition to give a target of 4 to 4.5% Al in the sheet. A full-size blend of powder with chemistry equivalent to Pack B plus 5% Al was then prepared.

4.3 Sheet Production

4.3.1 Processing of Ni-Cr-Al-ThO₂ Alloy

Eight sheets were processed four-at-a-time to nominally 20% weight gain in two cycles of 16 h each at 1522 K. An addition of 2% Al was made to the pack after completion of the first four sheets (i.e. prior to the initial 16 h cycle on the second batch of four sheets. A summary of the deposition data is given in Table XXXVI.

TABLE XXXVI. DUPLEX DEPOSITION DATA FOR SHEETS PROCESSED IN TASK IV

Sheet	Processing Time at 1522 K				
	16 h			32 h	
	kg/m ²	Total % Cr + Al	Microprobe Al Content (%)	kg/m ²	Total % Cr + Al
5-1	0.18	13.8	4.1	0.24	17.8
5-2	0.21	16.1	5.3	0.28	20.3
5-3	0.22	16.8	4.9	0.29	20.7
5-4	0.21	16.1	5.2	0.28	19.9
5-5	0.20	15.6	4.8	0.29	21.1
5-6	0.22	17.4	5.0	0.27	20.7
5-7	0.22	16.5	5.1	0.29	20.7
5-8	0.19	14.4	4.7	0.26	18.8

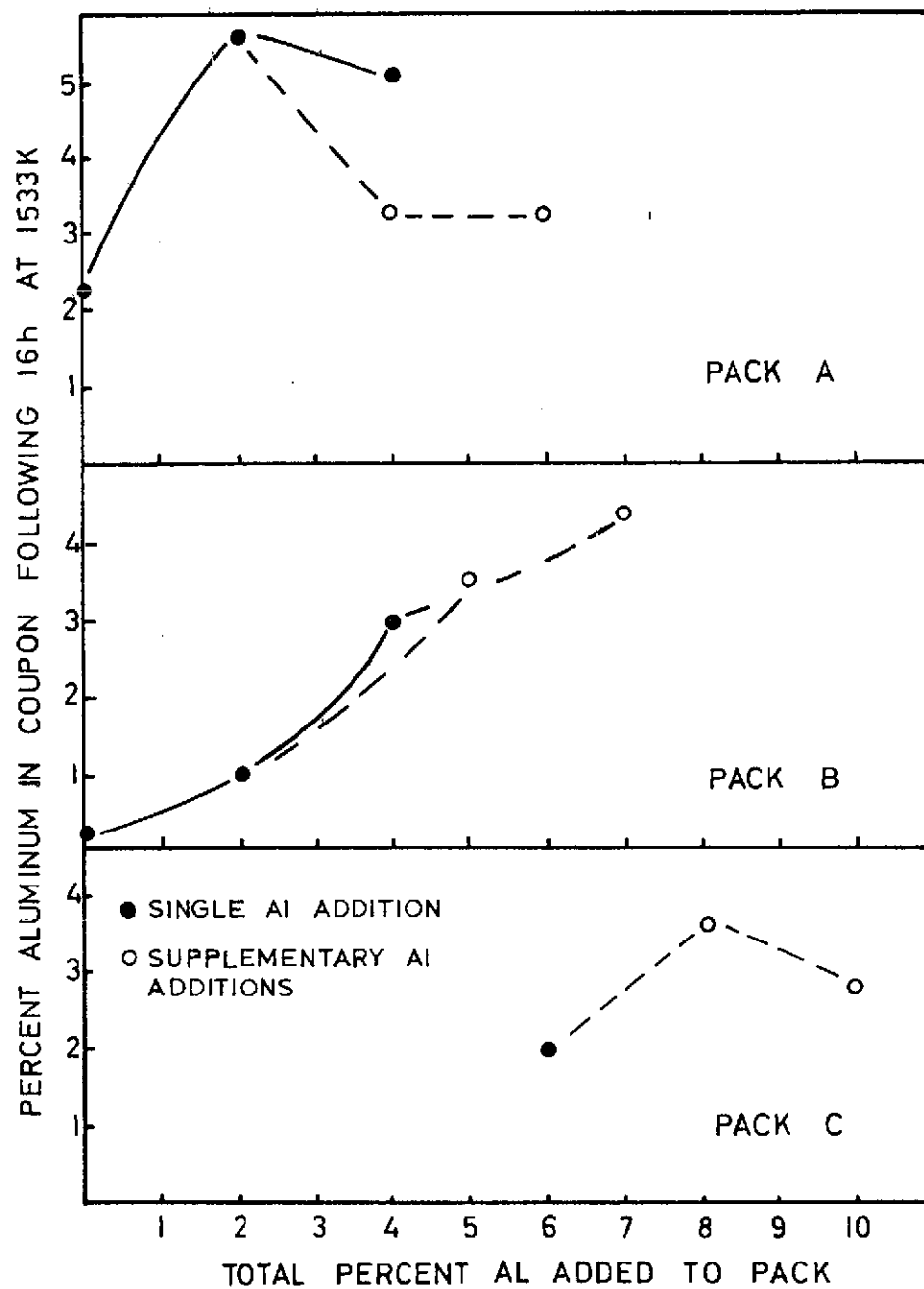


FIGURE 38. ALUMINUM CONCENTRATION IN SAMPLE COUPONS AS A FUNCTION OF PACK CHEMISTRY

Surface peeling, which would have been indicative of excessive aluminum deposition, was observed only on small areas of sheet 5-1 and 5-2 after the first cycle. No peeling occurred during the second cycle nor during subsequent annealing for 48 h at 1533 K.

Processing of the next batch of sheets (5-9 through 5-12), however, was not so successful. An addition of 2% Al was made to the pack and following the first 16 h cycle at 1522 K it was apparent that the resulting aluminum deposition was extremely high (weight gains were about 30% instead of the expected 15%). The sheets were very brittle and subsequent x-ray analysis showed that the TD Ni sheet had been converted almost entirely to the intermetallic phase NiAl. Figure 39 shows a typical section of one of these sheets.

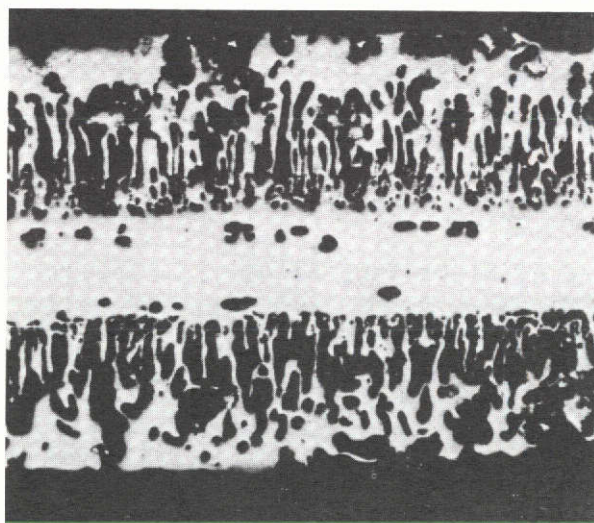
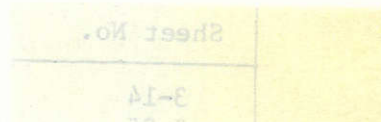


FIGURE 39. CROSS SECTION OF SHEET 5-12 SHOWING EFFECT OF EXCESSIVE ALUMINUM DEPOSITION (x100), UNETCHED



Examination of the thermodynamics involved in pack metallizing offers a logical explanation for the appearance of the intermetallic phase NiAl. With the assumption that aluminum is transferred from the metallizing pack to the Ni-ThO₂ sheet by a vapour transport mechanism, at equilibrium the activity of aluminum on the surface of the Ni-ThO₂ sheet will be equal to the activity of aluminum in the pack. Although the activity of aluminum in the Ni-Al and Cr-Al systems has not been measured at 1530 K, the aluminum activity in these systems has been measured at 1273 K, and these data are useful to illustrate the probable

behaviour during pack metallizing. Johnson et al (ref. 7) have shown the activity of aluminum in a Cr/5Al alloy (approximate pack composition) is about 10^{-3} . At equilibrium between the pack and the Ni-ThO₂ sheet, the activity of aluminum at the surface of the alloy sheet would also be 10^{-3} ; from the data of Steiner and Komarek (ref. 8) this aluminum activity corresponds to a Ni-50 at. % Al alloy - the intermetallic phase NiAl. Therefore it is quite possible to produce the NiAl intermetallic phase through use of a Cr/5Al alloy metallizing pack.

Evidently during the initial laboratory studies and sheet production runs, thermodynamic equilibrium between the Cr/Al pack and Ni-ThO₂ sheets was not achieved during every metallizing anneal. The inability to reach equilibrium could be due to surface reactions at the pack/vapour and/or vapour/Ni-ThO₂ alloy interfaces or insufficient vapour transport of aluminum from the pack to the Ni-ThO₂ sheet. Unfortunately the blocking reaction(s) which prevent equilibrium have not been identified; thus they cannot be controlled.

In order to remove the possibility of further NiAl formation during pack metallizing, a nickel-rich Ni/Cr/Al alloy should be used for the pack composition. Seltzer et al (ref. 3) have shown that aluminum can be introduced into TD NiCr (Ni-20Cr-2ThO₂) by an aluminizing process employing a Ni/10Cr/16Al pack. Therefore by simply increasing the chromium content in the Ni/Cr/Al pack alloy, it should be possible to introduce both aluminum and chromium into Ni-ThO₂ sheet.

4.3.2 Processing of Ni-Cr-ThO₂ Alloy

The Standard Process for production of the Ni-Cr-ThO₂ alloy was used to produce two sheets nominally 0.25 x 610 x 1270 mm and four sheets nominally 0.38 x 610 x 1270 mm. A summary of the deposition data is given in Table XXXVII and shows average chromium concentrations in the range 19.5 to 23.2% (the two thinner sheets contained the highest chromium contents).

TABLE XXXVII. CHROMIZING DATA FOR LOT 3 DS N1 SHEETS

Sheet No.	Gauge mm	Chromium	
		kg/m ²	%
3-14	0.25	0.34	22.4
3-25	0.25	0.34	23.2
3-19	0.41	0.46	19.6
3-20	0.41	0.47	20.4
3-22	0.41	0.48	20.6
3-23	0.41	0.48	20.9

4.3.3 Stretcher Leveling

The Ni-Cr-ThO₂ sheets were routinely stretched to adequate flatness using about 1.6% total strain. However, problems were again encountered in stretcher leveling of the Ni-Cr-Al-ThO₂ alloy. The edge preparation used in the Process Scale-Up portion of Task III to produce sheets 4-1 and 4-2 failed to eliminate sheet breakage. Several other approaches were tried including a 1 h annealing treatment at 1366 K followed by a rapid air cool (water quenching facilities were not available). A summary of the procedures used and their results is given in Table XXXVIII.

TABLE XXXVIII. SUMMARY OF PRE-LEVELING TREATMENTS APPLIED TO Ni-Cr-Al-ThO₂ SHEETS

Sheet	Pre-Leveling Treatment	Leveling Results
5-1	Sheared, sanded and annealed	Failed at 0.2% strain
5-2	Sheared and sanded	Failed at 0.5% strain
5-3	Sheared and sanded	Failed at 0.5% strain
5-4	Sanded	Failed at 0.5% strain
5-5	Sanded	Failed at 0.5% strain
5-6	Sanded and annealed	0.5% permanent strain
5-7	Sanded and annealed	0.5% permanent strain
5-8	Sanded and annealed	Failed at 0.5% strain

A permanent strain of 0.5% was not sufficient to provide a flatness comparable to that of the Ni-Cr-ThO₂ sheets but it was expected to be marginally acceptable for the subsequent grinding operation. Only five of the sheets (or portions thereof) were ultimately flat enough for grinding and were rough-sheared to the sizes given in Table XXXIX.

TABLE XXXIX. Ni-Cr-Al-ThO₂ SHEET SUITABLE FOR SURFACE GRINDING

Sheet	Size (mm)
5-2	625 x 1135
5-5	605 x 1040
5-6	625 x 1200
5-7	605 x 1200
5-8	605 x 1040

4.3.4 Surface Grinding

Processing of the Ni-Cr-ThO₂ sheets was routine. Good control of thickness and surface finish was achieved at both gauges using procedures established in Task II.

Processing of the Ni-Cr-Al-ThO₂ sheets, although showing an improvement over the Task III trials (sheets 4-1 and 4-2), was not up to the standards demonstrated for the Ni-Cr-ThO₂ sheets. Problems with non-uniform stock removal were related to inadequate flatness of the sheet stock and resulted in localized areas which either had residual surface porosity or were perforated by having been ground through the entire thickness. In addition, an overall problem with higher stock removal along the longitudinal center line of the sheets resulted in misleading gauge measurements (taken at the sheet edges) and subsequent over-grinding. This phenomenon appeared to be related to the presence of a harder, intermetallic phase in the surface layer along the edges of some of the sheets. Tables XL and XLI summarize the measured and calculated data related to the surface finish and gauge control for the Ni-Cr-Al-ThO₂ (5-series) and Ni-Cr-ThO₂ (3-series) sheets. Gauge measurements were obtained at about 150 mm intervals along the sheet edges.

TABLE XL. SURFACE FINISH AND GAUGE CONTROL ON Ni-Cr-ThO₂ AND Ni-Cr-Al-ThO₂ SHEETS

Sheet Number	Gauge (mm)		Surface Finish RMS, nm
	Range	Mean	Side 1/Side 2
5-2	0.246 - 0.294	0.266	280/460
5-5	0.223 - 0.272	0.248	360/510
5-6	0.200 - 0.264	0.233	300/410
5-7	0.190 - 0.272	0.241	430/530
5-8	0.228 - 0.302	0.272	300/380
3-14	0.241 - 0.279	0.264	300/360
3-25	0.241 - 0.259	0.251	330/380
3-19	0.353 - 0.406	0.379	300/380
3-20	0.356 - 0.404	0.381	250/300
3-22	0.366 - 0.424	0.390	280/360
3-23	0.351 - 0.406	0.384	280/300

TABLE XLI. COMPARISON OF ACTUAL AND THEORETICAL WEIGHTS OF
Ni-Cr-ThO₂ and Ni-Cr-Al-ThO₂ SHEETS

Sheet Number	Actual Sheet Weight kg	Theoretical Sheet Weight ^a kg	% Deviation from Theoretical Weight
5-2	1.36	1.26	+ 8.7
5-5	1.05	1.17	-11
5-6	1.11	1.34	-17
5-7	1.23	1.36	- 9.7
5-8	1.23	1.17	+ 4.7
3-14	1.61	1.55	+ 3.9
3-25	1.5	1.55	- 2.6
3-19	2.28	2.30	- 1
3-20	2.36	2.32	+ 1.9
3-22	2.48	2.32	+ 7.1
3-23	2.38	2.32	+ 3.1

a. Calculated on the basis of nominal gauges 0.25 or 0.38 mm and theoretical densities of 8.49 g/cm³ for Ni-20Cr-2ThO₂ and 7.82 g/cm³ for Ni-16Cr-5Al-2ThO₂.

With the exception of two small areas on sheet 3-22 all gauge measurements on the Ni-Cr-ThO₂ sheets were within $\pm 10\%$ of the nominal gauge. The deviations from theoretical weights were in good agreement with the mean gauge values and generally reproduced those obtained earlier in the programme. The large difference in the deviation values for the Ni-Cr-Al-ThO₂ sheets, however, reflected the difficulties encountered with non-uniform stock removal. The large negative deviation for sheet 5-6 indicated that the actual mean gauge was closer to 0.21 mm than the tabulated value of 0.233 mm.

4.4 Evaluation of Alloy Sheets Produced in Task IV

4.4.1 Inspection and Sampling

All sheets were inspected for surface flaws and general integrity prior to the shearing of samples for material characterization tests. All of the Ni-Cr-ThO₂ sheets were free of visual defects but, as mentioned previously, the aluminum-modified sheets were plagued with several defects. A summary of the inspection results for the latter sheets appears in Table XLII.

TABLE XLII. INSPECTION RESULTS OF Ni-Cr-Al-ThO₂ SHEETS

Sheet Number	Comments
5-2	Both sides showed extensive residual surface porosity primarily on one end of the sheet.
5-5	One side good but other showed a few isolated areas of residual porosity.
5-6	Both sides good.
5-7	One side good but other with small area of residual porosity.
5-8	Residual porosity on both sides primarily along longitudinal edges. One large longitudinal flaw about 381 mm long located at the center of one-half of the sheet. Caused by grinding through the entire thickness of the sheet.

Sheets 5-2 and 5-8 were selected for the destructive testing portion of the evaluation programme. A layout of the location of samples for the mechanical property tests is given in Figure 40. The Ni-Cr-ThO₂ sheets were not destined for an intensive evaluation programme and samples were therefore obtained only from the ends of several sheets.

4.4.2 Chemical Analyses

Sheets 5-2 and 5-8 were submitted for chemical analyses and electron microprobe examination. The resulting analyses for chromium and aluminum concentrations in sheet 5-8 are shown in Figure 41. Agreement between the results from the two analytical techniques was acceptable but the target concentration levels of $16 \pm 2\%$ Cr and $4.5 \pm 1\%$ Al were not achieved in this sheet. The general trend indicated a high aluminum concentration near the longitudinal centerline of the sheet and lower aluminum content in the areas where the surface intermetallic had been observed (at the time of surface grinding). Other analytical results are summarized as follows:

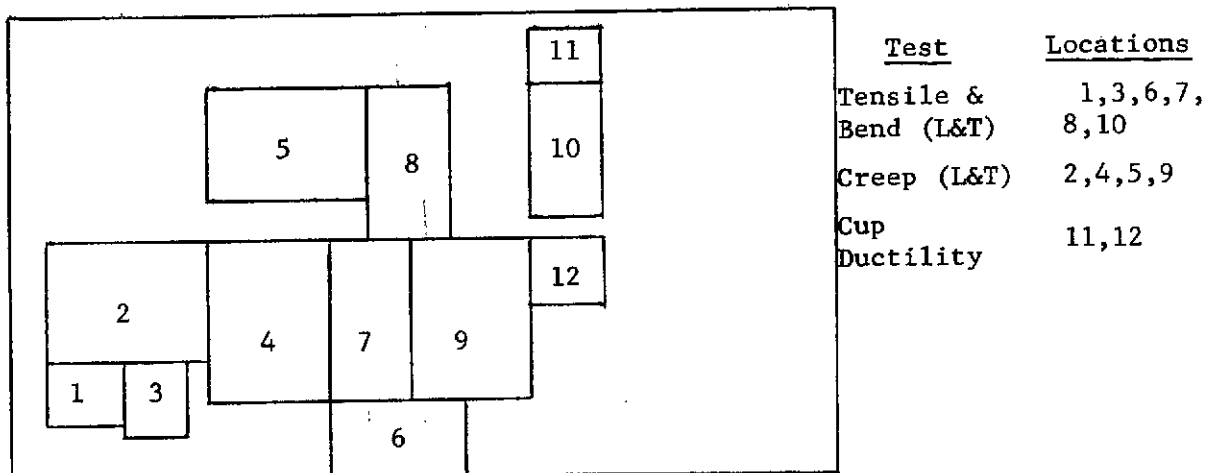
TABLE XLIII. CHEMICAL COMPOSITION OF Ni-Cr-Al-ThO₂ and Ni-Cr-ThO₂ SHEETS PROCESSED IN TASK IV

Concentration (wt. %)										
Sheet	ThO ₂	Total O ₂	S	C	Fe ^a	Cu ^b	Mn ^b	Cr ^c	Al ^c	Ni
5-2	1.92	0.27	0.0047	0.0122	0.088	0.003	0.03	13.5	7	bal.
5-8	1.92	0.27	0.0033	0.0084	0.087	0.01	0.07	12.5	7	bal.
3-22	1.7	0.21	0.0085	0.004	0.09	0.005	0.08	20	0	bal.

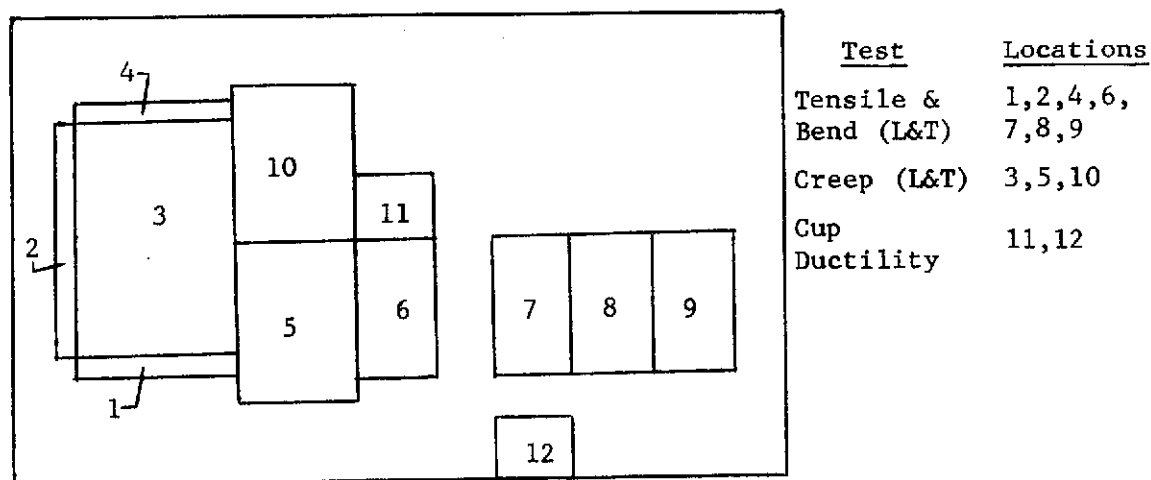
a. By atomic absorption.

b. By emission spectrograph.

c. Estimated averages.



(a) Sheet 5-2; Nominal size 600 x 1100 mm



(b) Sheet 5-8; Nominal size 600 x 1000 mm

FIGURE 40. LOCATION OF SAMPLES FOR MECHANICAL PROPERTY TEST PROGRAMME

		14.1 (12.9)
		12.8 (11.5)
11.2 (12.7)	12.3 (12.6)	12.3 (11.4)
		12.1 (11.5)
		14.2 (14.4)

(a) Chromium Concentration in Weight Percent

		5.8 (6.0)
		6.7 (7.4)
7.1 (7.4)	7.3 (7.9)	7.3 (7.7)
		6.9 (7.8)
		6.0 (7.3)

(b) Aluminum Concentration in Weight Percent

FIGURE 41. ELECTRON MICROPROBE AND WET CHEMICAL ANALYTICAL RESULTS AS A FUNCTION OF LOCATION IN SHEET 5-8 (NOMINAL SHEET SIZE 600 x 1000 mm). PARENTHETICAL VALUES ARE WET CHEMICAL RESULTS.

The ThO₂ sizes as determined by the x-ray line broadening technique were 21.5 nm for the Ni-Cr-Al-ThO₂ sheets and 20 nm for Ni-Cr-ThO₂ sheet 3-22 which compare well with the 20 to 23 nm determined for chromized DS Ni or TD Ni (Task II).

4.4.3 Mechanical Property Testing

With the exception of the high temperature creep studies all evaluation was done at Sherriitt Gordon. Creep samples were forwarded to Metcut Research Associates in Cincinnati, Ohio to be evaluated under NASA Contract NAS 3-15558. The stresses to produce 0.1, 0.2 and 0.5% total plastic creep deformation in 100 h at 1366 K were determined for samples in the longitudinal and transverse orientation. The results are given in Appendix C.

A measure of the formability of the Ni-Cr-Al-ThO₂ alloy was obtained using cup ductility, bend ductility and springback tests. The results from this study are given in Table XLIV along with comparative values for sheet 2-13 (chromized TD Ni).

TABLE XLIV. FORMABILITY DATA

Sample	Gauge mm	Cup Height at Fracture ^a mm	105° Bend (radius)		Springback 12.7 mm test length	
			Long.	Trans.	Long.	Trans.
5-2	0.25	4.8	1.5t	8t	29°	29°
5-8	0.25	5.3	1.5t	8t	-	-
2-13	0.38	8.1	1t	1t	15°	-

a. Olsen cup tester; diameter of indenting ball 20 mm; diameter of clamped region 36 mm.

The poor bend ductility in the transverse direction was related to the relatively coarse surface finish on the aluminum-modified sheets (RMS generally greater than about 410 nm). Removal of the coarse grinding marks by hand polishing allowed transverse samples to pass the 1.5t bend test. The higher springback values and lower cup heights for the aluminum-modified alloy are indicative of lower formability.

The tensile properties of sheets 5-2 and 5-8 were determined at five temperatures from room temperature to 1366 K. Duplicate samples were tested at each temperature (one sample from each sheet) and the values shown in Figure 42 are the average. The tensile properties of this alloy were exceptionally high over the entire temperature range, particularly in the 1033 to 1366 K region. For comparison, typical properties of Nimonic 80A, a commercial precipitation-hardened nickel-base superalloy and a powder metallurgy Ni-Cr-ThO₂ material (laboratory fabricated) are shown in Table XLV.

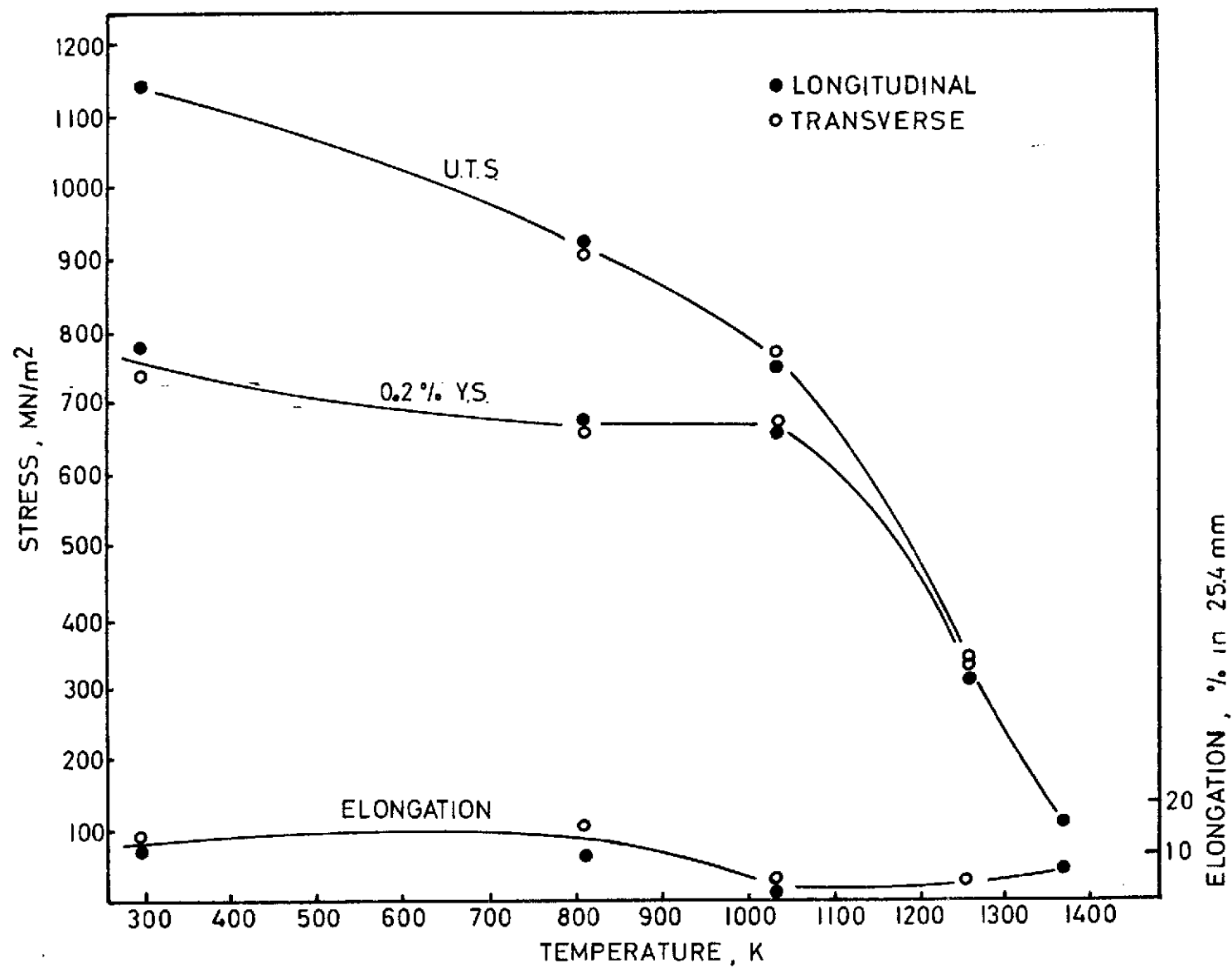


FIGURE 42. TENSILE PROPERTIES OF Ni-Cr-Al-ThO₂ SHEETS 5-2 AND 5-8

TABLE XLV. COMPARATIVE ULTIMATE TENSILE STRENGTHS AS A
FUNCTION OF TEMPERATURE (REF. 9)

Temperature K	Ni-Cr-Al-ThO ₂ MN/m ²	Nimonic 80A MN/m ²	Ni-Cr-ThO ₂ MN/m ²
294	1140	1035	760
922	825	795	415
1033	760	415	207
1255	345	104	138
1366	110	27.5	117

The stress rupture properties of the Ni-Cr-Al-ThO₂ alloy were determined at four temperatures in the range 811 to 1366 K. An approximately equal number of samples was tested from each of sheets 5-2 and 5-8 and the results are given in Figure 43. Elongations at failure were in the range 2 to 4% with the exception of the 811 K tests which showed up to 8% elongation at intermediate times. The material was isotropic at the two low temperatures but at 1255 and 1366 K the strength was lower in the transverse direction. Additionally, the slope of the curves at temperatures of 1033 K and above was more negative than at 811 K which was presumably due to coarsening and dissolution of the γ' present in the alloy.

Only a limited amount of testing was conducted on the Ni-Cr-ThO₂ sheets and the results are given in Table XLVI.

TABLE XLVI. TRANSVERSE MECHANICAL PROPERTIES OF Ni-Cr-ThO₂ SHEET 3-22

Room Temperature					1366 K			
Sheet	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	105° Bend Test	0.2% YS MN/m ²	UTS MN/m ²	Elong. % in 25.4 mm	Stress Rupture Life
3-22	600	785	14	1t	100	108	3	100 h @ 31 MN/m ²

4.4.4 Metallography and Electron Microscopy

Typical microstructures of the Ni-Cr-ThO₂ and Ni-Cr-Al-ThO₂ alloys produced in Task IV are shown in Figures 44 and 45. The Ni-Cr-Al-ThO₂ structure has retained the highly elongated grains originally present in the TD Ni and the ThO₂-free bands are readily visible (white streaks). The Ni-Cr-ThO₂ microstructure is much the same as that observed in the Task II studies (Section 2.6.3).

C~

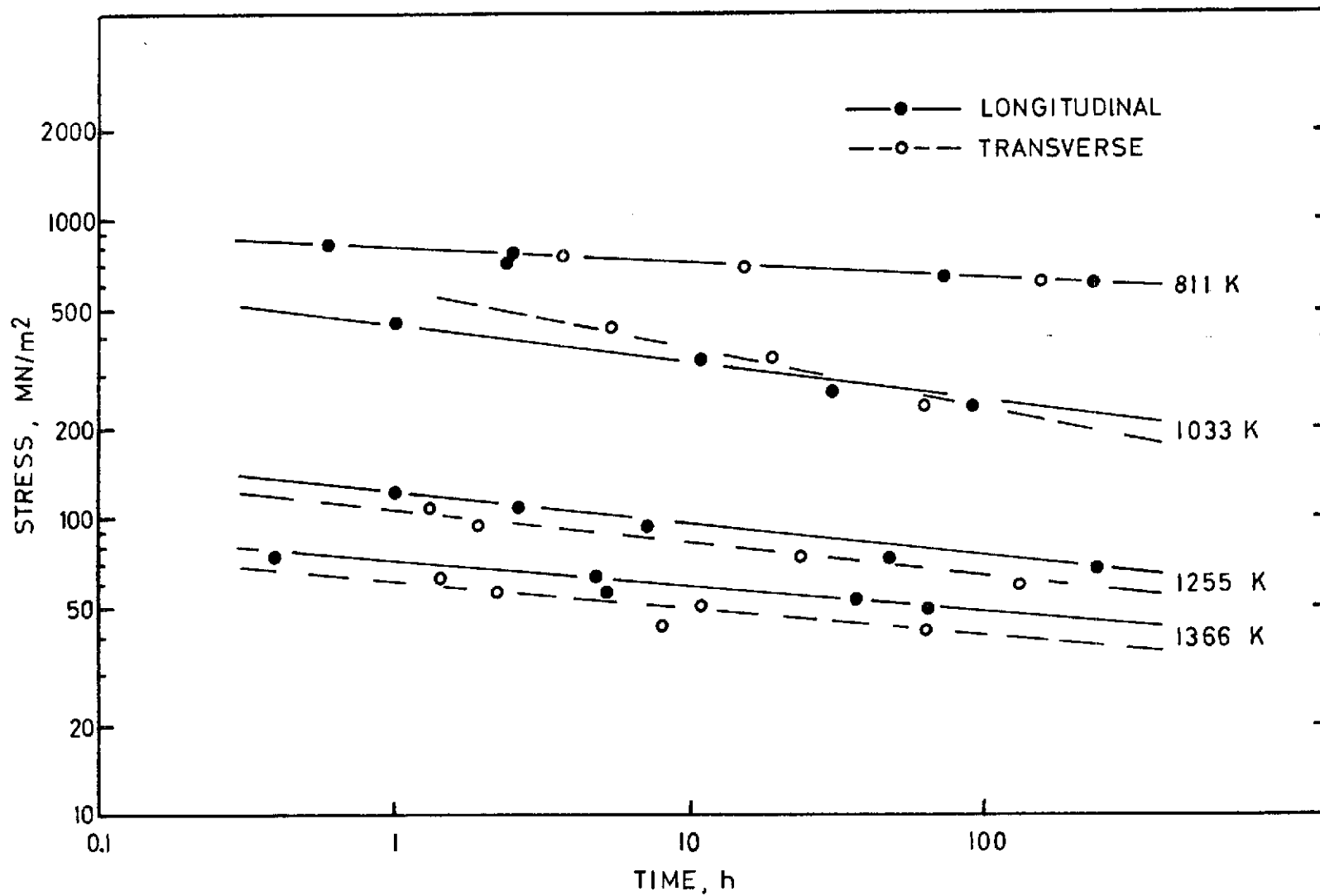
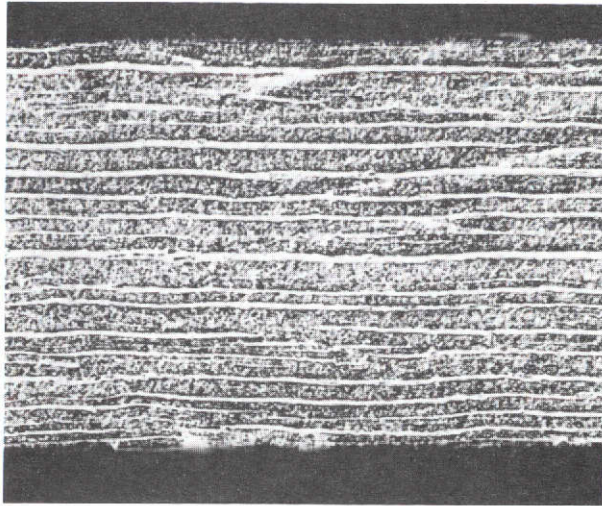
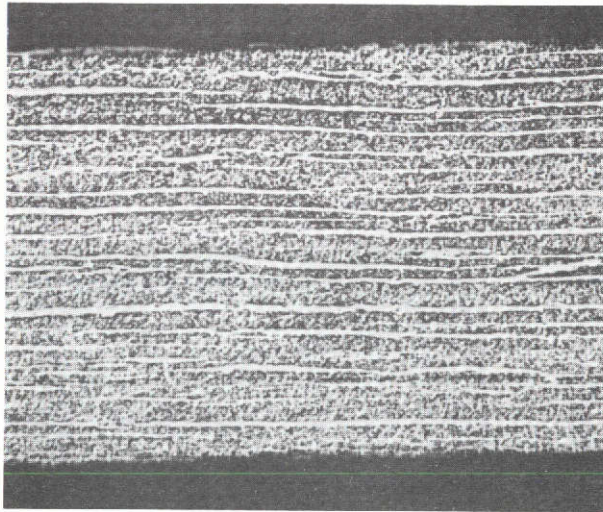


FIGURE 43. STRESS RUPTURE PROPERTIES OF Ni-Cr-Al-ThO₂ SHEETS 5-2 AND 5-8



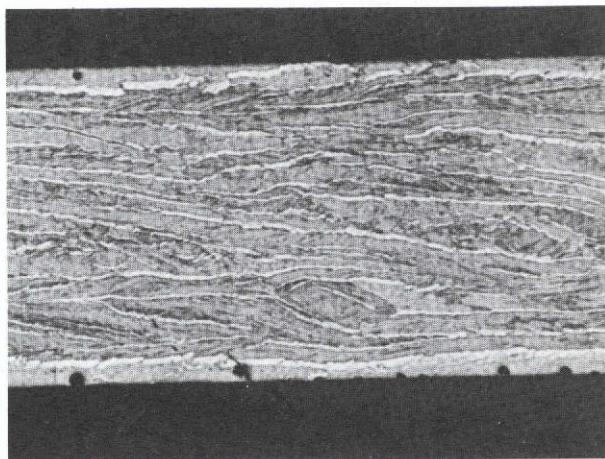
a) Longitudinal Cross Section



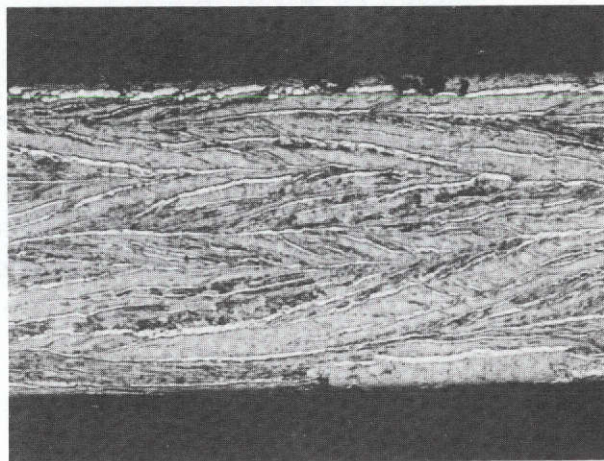
b) Transverse Cross Section

FIGURE 44. MICROSTRUCTURE OF Ni-Cr-Al-ThO₂ SHEET 5-8 (x250)
ETCHANT: 3% OXALIC ACID, ELECTROLYTIC

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a) Longitudinal Cross Section



b) Transverse Cross Section

FIGURE 45. MICROSTRUCTURE OF Ni-Cr-ThO₂ SHEET 3-22 (x100)
ETCHANT: 3% OXALIC ACID SOLUTION, ELECTROLYTIC

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Transmission electron micrographs were obtained from several positions on Ni-Cr-Al-ThO₂ sheet 5-8. The distribution of ThO₂ particles is generally quite good, but ThO₂-deficient areas such as shown in Figure 46 b) are common. A peculiar duplex precipitate structure was observed in samples taken from areas known to be higher in aluminum concentration (primarily near the centerline of the sheet) and is shown in Figure 47. The very fine γ' precipitate was actually present in many other areas but the large blocky form was restricted to areas near the sheet center. The fine γ' particles could have formed during the cooling cycle of either the homogenizing anneal or the pre-leveling anneal but as both γ' forms were also observed in sheet 5-2 (which was not given a pre-leveling anneal) the former is more likely. The reason for the appearance of the blocky form, however, is not apparent unless the local aluminum concentration is sufficiently high to allow the formation of γ' at the homogenizing temperature (1533 K).

4.4.5 Oxidation Resistance

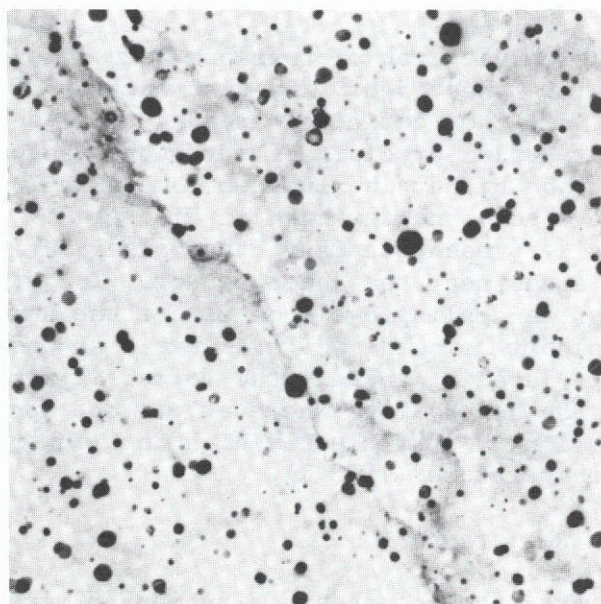
Samples from each of sheets 5-2 and 5-8 were tested in the dynamic oxidation test facility at 1366 K and 1477 K. The test cycle was the same as that used previously, namely 50 h of testing with cycles of 1200 s at temperature and 15 s cooling. Weight changes were obtained at the 16 h, 32 h and 50 h points and are summarized in Table XLVII.

TABLE XLVII. SUMMARY OF CYCLIC DYNAMIC OXIDATION TEST RESULTS FOR TASK IV Ni-Cr-Al-ThO₂ ALLOYS

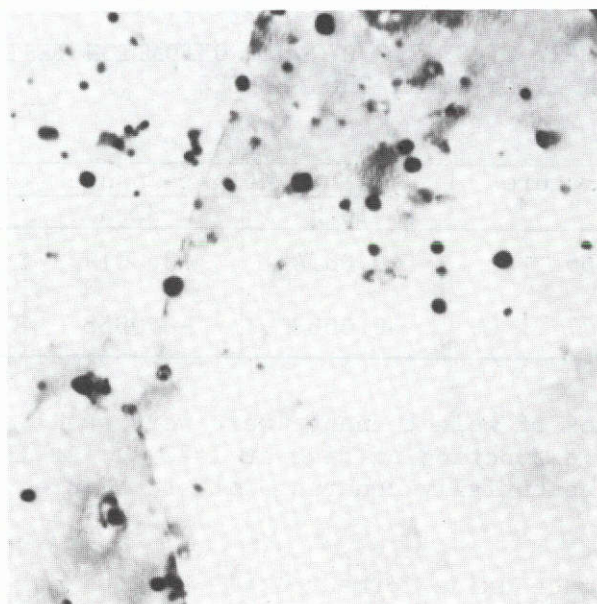
Temperature K	Weight Change (kg/m ²)		
	16 h	32 h	50 h
1366	+0.0024	+0.0019	+0.0024
1477	-0.0033	-0.0058	-0.0071

The observed values of weight change were very small at both temperatures and were negative and a function of time at 1477 K. At 1366 K the weight change was positive and essentially constant with time (precision of about +0.0003 kg/m²).

The surface oxide formed on all samples was identified by x-ray diffraction techniques as Al₂O₃ with small amounts of NiAl₂O₄. Cross-sections of test samples are shown in Figures 48 and 49.



a) Uniform ThO_2 Distribution



b) ThO_2 -deficient Zones

FIGURE 46. TRANSMISSION ELECTRON MICROGRAPHS OF Ni-Cr-Al- ThO_2 SHEET 5-8 (x20,000)

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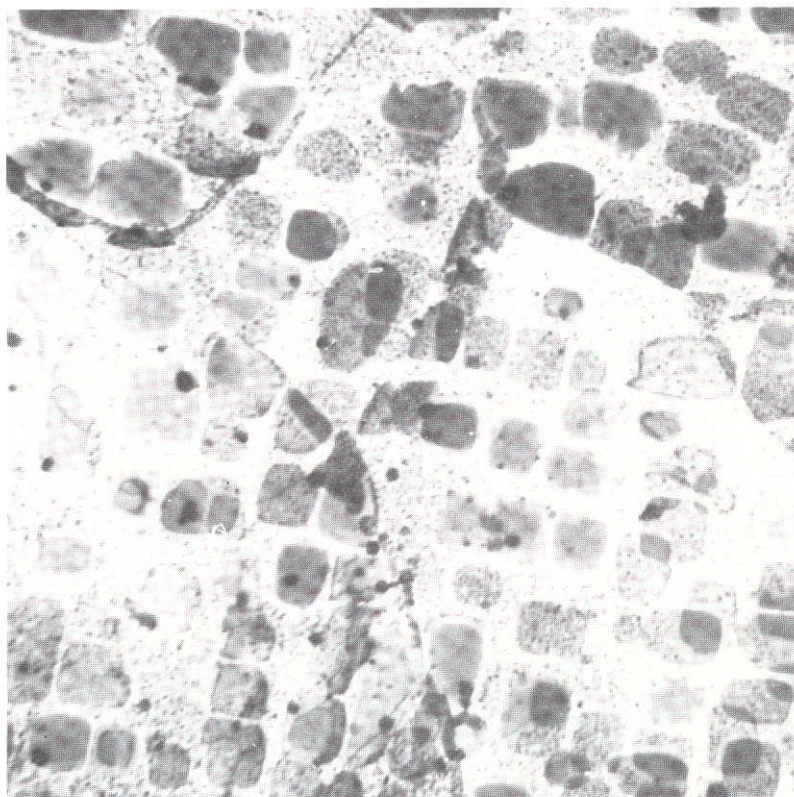
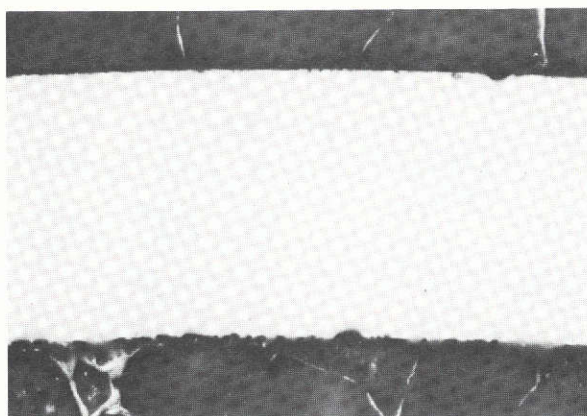
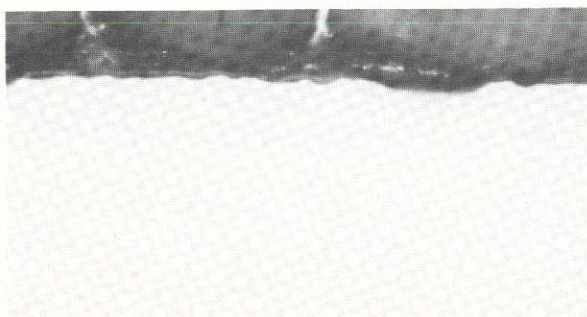


FIGURE 47. TRANSMISSION ELECTRON MICROGRAPH SHOWING DUPLEX γ' PRECIPITATE IN Ni-Cr-Al-ThO₂ SHEET 5-8 (x20,000)

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a) Sample Thickness (x150)



b) Surface Oxide (x400)

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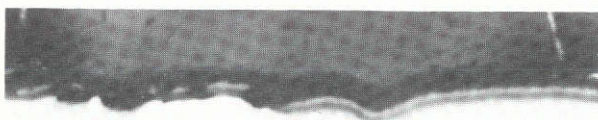
FIGURE 48. CROSS SECTION OF SAMPLE OF Ni-Cr-Al-ThO₂ SHEET 5-8 AFTER 50 h CYCLIC DYNAMIC OXIDATION AT 1366 K, UNETCHED



a) Sample Thickness (x150)



b) Surface Oxide (x400)



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FIGURE 49. CROSS SECTION OF Ni-Cr-Al-ThO₂ SHEET 5-8 AFTER 50 h CYCLIC DYNAMIC OXIDATION AT 1477 K, UNETCHED

4.5 Task Completion

The following sheet material was sent to NASA-Lewis:

<u>Nominal Composition</u>	<u>Number of Sheets</u>	<u>Nominal Size mm</u>	<u>Weight kg</u>
Ni-13Cr-6Al-2ThO ₂	3	0.24 x 600 x 1100	3.4
Ni-20Cr-2ThO ₂	2	0.25 x 600 x 1200	3.1
	4	0.38 x 600 x 1200	9.5

A reproducible process for the aluminum-modified alloy was not developed. A Standard Process for the production of Ni-Cr-ThO₂ sheets was described in Task II (Section 2.5) but since the greater portion of Task IV was concerned with the aluminum-modified alloy, a suitable quantity of the optimum Ni-Cr-ThO₂ product was not produced. However, based on the data generated on the importance of microstructure and elevated temperature strength of the Ni-ThO₂ sheet used in the process, a tentative product specification for a Ni-Cr-ThO₂ sheet material was produced and is given in Appendix D.

SUMMARY OF RESULTS

The objective of the programme was to develop a pack diffusion and alloying process for the production of thin gauge Ni-Cr-ThO₂ or Ni-Cr-Al-ThO₂ sheet which could meet the technical requirements of thermal protection systems on space shuttle vehicles. The process involved the following steps: (1) elevated temperature deposition of chromium (or chromium plus aluminum) from a powder pack onto a wrought Ni-2ThO₂ sheet, (2) homogenization of the chromium (or chromium plus aluminum) by extended heat treatment, and (3) flattening and grinding to produce finished product.

The Ni-Cr alloy process development followed the steps of small scale studies using sheet stock 305 x 460 mm in size, scale-up to produce sheets 610 x 1220 mm, process reproducibility and material characterization. The small scale studies were conducted with a Cr/5Y₂O₃ powder pack and three different Ni-2ThO₂ sheet materials. A requirement for a fine grain elongated microstructure and a high degree of sheet flatness was demonstrated as well as the critical dependence of the mechanical properties of the Ni-Cr-ThO₂ alloy on the properties of the Ni-ThO₂ material. A wide-belt abrasive grinding process was defined to provide the required stock removal and the mandatory use of a coolant during grinding was indicated.

The scale-up studies were conducted with both DS Ni and TD Ni sheet stock and resulted in definition of the processing conditions for the production of material in the gauge range 0.25 to 0.51 mm. Laboratory studies showed that neither the chromium particle size (150 to 400 mesh) nor the surface condition of the Ni-ThO₂ material (coarse versus fine surface finish and oily versus acid cleaned surfaces) were important variables in the process. A standard production process was developed which included the critical parameters of a slow preheat during chromizing (to minimize temperature gradients in the pack), use of a light gauge retort material (to minimize distortion during temperature changes), use of stretcher leveling rather than roller leveling (insufficient flatness) or cold rolling (low recoveries) and the use of worn grinding belts during the last pass to provide a surface finish of less than 410 nm RMS. The process was generally reproducible. However, non-uniform stock removal during surface grinding led to thickness variations exceeding the goal of $\pm 10\%$ of the target gauge. Evidence of creep degradation was shown during the evaluation of stress rupture properties and the severity was related to the orientation of the ThO₂-free bands with respect to the stress axis: bands parallel to the stress axis resulted in better rupture properties than did bands inclined to the stress axis. (ThO₂-free bands are an unavoidable feature of the diffusion of chromium normal to grain boundaries).

Development of a similar process for the production of a Ni-Cr-Al-ThO₂ alloy was also studied. Preliminary investigations demonstrated that the duplex Cr/Al deposition process was more difficult to control. The aluminum deposition was critically dependent on aluminum activity in the pack and the aluminum diffusion within the in-process sheet was more dependent on composition than was the chromium diffusion. A screening programme led to selection of an alloy containing 16% Cr and 4% Al rather than 5% Al. The lower aluminum

content appeared to yield better ductility and no water quench was required to suppress precipitation of the gamma-prime (γ') intermetallic phase. Mechanical properties of the alloys produced in the screening phase exceeded the goals for the programme but during subsequent scale-up to 610 x 1220 mm sheet, major reproducibility problems were encountered and it was discovered that certain TD Ni microstructures when chromized and aluminized were susceptible to severe creep degradation.

The material characterization studies, however, were conducted primarily on the aluminum-modified alloy because of sustained interest in this more oxidation-resistant material. Higher strength TD Ni enabled production of an aluminum-modified alloy which possessed excellent strength properties in the temperature range 300 to 1370 K and excellent high temperature oxidation resistance. Control of the duplex Cr/Al deposition process however, was not optimized and this, combined with high in-process losses, led to inordinately low recoveries. The material requirements were met with Ni-Cr-Al-ThO₂ sheet and with Ni-Cr-ThO₂ sheet produced using the established standard process (3.4 kg of Ni-Cr-Al-ThO₂ sheet and 12.6 kg of Ni-Cr-ThO₂ sheet in sizes 0.24 to 0.38 x 600 x 1200 mm were shipped to NASA-Lewis).

APPENDIX A

Description of Chromizing Furnace and Hydrogen Purifier

The furnace used in the programme was designed and built by Canefco Limited of Scarborough, Ontario and was purchased on Canadian Defence Research Board Grant No. 7510-66.

The furnace hot zone was electrically heated with molybdenum elements giving 140 KW output and required an inner lining of high purity Al_2O_3 refractories ("Insulpure" from Babcock and Wilcox) to withstand the low dew point hydrogen atmosphere. Maximum operating temperature was 1616 K with continuous service at 1560 K. Dimensions of the hot zone were nominally 0.5 x 1.2 x 3 m and a 3-zone proportioning control system was used to provide temperature uniformity (specified to be ± 5 K throughout the hot zone). An attached cooling zone, separated from the hot zone by a refractory lined door, provided controlled atmosphere cooling although dew points less than about 240 K were not possible. Placement and retraction of the furnace charge was achieved with a push-pull stoker mechanism positioned at the cooling zone end of the furnace.

The hydrogen purification system (also purchased under DRB Grant No. 7510-66) was based on a palladium-silver alloy diffusion cell manufactured by Engelhard Industries, New Jersey. Advertised capacity was 16 m^3/h of ultrapure hydrogen at 0.035 MPa (gauge) and a measured dew point of about 220 K.

APPENDIX B

Programme Specification Goals

Ni-Cr-ThO₂ and Ni-Cr-Al-ThO₂ Sheet

0.25 to 0.51 mm Gauge

1. Chemical Composition (wt. %)

	<u>Ni-Cr-ThO₂</u>	<u>Ni-Cr-Al-ThO₂</u>
ThO ₂	1.60 - 2.40	1.60 - 2.40
Cr	18.0 - 22.0	14.0 - 18.0
C	0.005 maximum	0.005 maximum
S	0.005 maximum	0.005 maximum
Al	0	3.5 - 5.5
Ni	Balance	Balance

2. Mechanical Properties (minimum properties parallel or normal to rolling direction)

2.1 At Room Temperature

Yield Strength, MN/m ²	415
Ultimate Tensile Strength, MN/m ²	550
Elongation, % in 25.4 mm	10

2.2 At 1366 K

Yield Strength, MN/m ²	83
Ultimate Tensile Strength, MN/m ²	97
Elongation, % in 25.4 mm	3
Stress to rupture in 100 h, MN/m ²	27.6
Elongation, % in 25.4 mm	2

3. Bend Ductility

105° bend angle using 2t bend radius without cracking
(3t for Ni-Cr-Al-ThO₂)

4. Dimensional Tolerances

4.1 Flatness within 6%

4.2 Surface finish - 410 nm RMS or better

4.3 Thickness variations within a sheet and from sheet to sheet produced at a specified gauge shall not exceed ±10%.

APPENDIX C

Creep Properties of Ni-Cr-Al-ThO₂ Sheets Produced in Task IV

The creep properties of two sheets produced in this programme were measured at Metcut Research Associates, Cincinnati, Ohio, under contract NAS 3-15558. Samples from sheets 5-2 and 5-8 were tested in both the longitudinal and transverse directions at 1366 K. The interpolated values for stresses to cause specific creep strains in 100 h are given in Table XLVIII and the raw data are tabulated in Table II. The data suggested that higher stresses would be required to give 0.1 and 0.2% creep strain in sheet 5-8 than with sheet 5-2 but this difference was not so apparent at higher strains.

Based on these results and the limited data available for the Fansteel TD NiCrAl alloy (ref. 10), it was concluded that the alloy produced in this programme was considerably more creep resistant than the 5% Al Fansteel alloy (0.5% creep in 100 h at 13.8 MN/m²) and slightly better than the 3.5% Al alloy (0.5% creep in 100 h at 27.6 to 34.5 MN/m²).

TABLE XLVIII. INTERPOLATED VALUES FOR STRESS LEVEL TO
PRODUCED SPECIFIC CREEP STRAIN IN 100 h

Creep Strain %	Stress Level, MN/m ²			
	Sheet 5-2		Sheet 5-8	
	Longitudinal	Transverse	Longitudinal	Transverse
0.1	20	19	30	30
0.2	26	27	32	32
0.5	33	34	35	36

TABLE II. CREEP DATA FOR Ni-Cr-Al-ThO₂ SHEETS 5-2 AND 5-8
TESTED AT 1366 K

Specimen No.	Stress MN/m ²	Creep Strain (%) at Time Shown (h)						Test Duration h
		0.1	1	10	50	100	Final	
5-2-5L1	20.0	0.02	0.04	0.06	0.09	0.10	0.10	112.1
5-2-5L2	20.0	0.01	0.02	0.03	0.04	0.04	0.04	101.3
5-2-2L3	24.1	0.01	0.03	0.08	0.14	0.19	0.19	100.0
5-2-2L2	31.0	0.03	0.05	0.09	0.18	0.26	0.26	100.6
5-2-5L3	33.1	0.01	0.08	0.14	0.19	0.25	0.25	99.9
5-2-2L1	34.5	0.04	0.09	0.23	0.41	0.54	0.54	101.2
5-8-3L3	31.0	0.02	0.03	0.07	0.11	0.13	0.13	100.0
5-8-3L4	31.0	0.01	0.04	0.12	0.24	0.33	0.35	112.7
5-8-3L5	33.1	0.01	0.02	0.04	0.06	0.07	0.07	101.3
5-8-3L6	33.1	0.01	0.03	0.09	0.19	0.26	0.26	102.1
5-8-3L1	34.5	0.01	0.05	0.11	0.23	0.34	0.34	102.0
5-8-3L2	36.5	0.02	0.07	0.20	0.40	0.71	0.82	112.1
5-2-9T2	17.2	0.01	0.02	0.03	0.05	0.07	0.07	102.9
5-2-4T3	20.7	0.02	0.03	0.06	*	0.21	0.22	113.0
5-2-9T3	20.7	0.01	0.03	0.07	0.12	0.15	0.15	102.0
5-2-4T2	27.6	0.03	0.04	0.07	0.12	0.21	0.21	101.3
5-2-9T1	31.0	0.03	0.06	0.11	0.18	0.26	0.28	111.1
5-2-4T1	34.5	0.03	0.08	0.19	0.36	0.47	0.49	112.1
5-8-10T1	29.7	0.01	0.03	0.06	0.09	0.10	0.10	112.8
5-8- 5T3	31.0	0.02	0.03	0.07	0.13	0.17	0.17	100.0
5-8-10T2	33.1	0.02	0.05	0.12	0.23	0.30	0.30	99.9
5-8- 5T1	34.5	0.02	0.07	0.12	0.21	0.33	0.48	112.2
5-8- 5T2	36.5	0.02	0.07	0.15	0.26	0.40	0.43	112.1
5-8-10T3	36.5	0.02	0.06	0.16	0.40	1.43	1.48	102.1

* Indicated jump in strain rate between 45 and 51.9 h.

APPENDIX D

Sherritt Gordon Tentative Product Specification

DS Nickel-Chromium Sheet

1. Scope

This specification covers composition, property, surface and dimensional requirements for Sherritt DS NiCr Sheet.

2. Chemical Composition

The chemical composition, as determined by ASTM standard analytical procedures, shall conform to the following limits:

<u>Constituent</u>	<u>Minimum Weight Percent</u>	<u>Maximum Weight Percent</u>
Thoria (ThO ₂)	1.60	2.40
Chromium	18.0	22.0
Carbon	-	0.020
Sulphur	-	0.020
Nickel	By difference	

3. Mechanical Properties

3.1 Room Temperature Properties: Sheet supplied under this specification shall conform to the following minimum requirements when tested at room temperature transverse to the final rolling direction in accordance with procedures described in Section 5.1.

<u>0.2% Offset Yield Stress MN/m²</u>	<u>Ultimate Tensile Strength MN/m²</u>	<u>Elongation in 25.4 mm %</u>
500	700	10

3.2 Elevated Temperature (1366 K in air) Tensile Properties: Sheet supplied under this specification shall conform to the following minimum requirements when tested at 1366 K in air transverse to the final rolling direction in accordance with the procedures described in Section 5.2.

<u>0.2% Offset Yield Stress MN/m²</u>	<u>Ultimate Tensile Strength MN/m²</u>	<u>Elongation in 25.4 mm %</u>
To be reported	83	2

3.3 Stress Rupture (1366 K in air) Properties: Sheet supplied under this specification shall conform to the following minimum requirements when tested at 1366 K in air transverse to the final rolling direction in accordance with the procedure in Section 5.3.

Stress <u>MN/m²</u>	Life <u>h</u>	Elongation in 25.4 mm <u>%</u>
27.5	20	To be reported

3.4 Bend Tests: Material shall withstand, without cracking, bending at room temperature through an angle of 105 degrees around a radius equal to a bend factor of two times the nominal thickness of the material, with the bend axis either perpendicular or parallel to the direction of rolling.

4. Surface and Dimensional Requirements

4.1 Material shall be supplied with a ground surface finish (maximum 510 nm RMS).

4.2 By visual inspection, the material shall be free of any evidence of contamination and internal or external imperfections detrimental to fabrication, appearance or performance of parts.

4.3 The material shall be free of surface imperfections which reduce the thickness below the minimum permitted by the thickness tolerance. Imperfections of less than this depth, but greater than 0.013 mm, shall be permitted, provided their number is not more than 50 per square metre.

4.4 Tolerances

4.4.1 Thickness tolerance shall be $\pm 10\%$ of nominal gauge. Measurements shall be taken at least 10 mm from the edge of the sheet.

4.4.2 Width and length tolerances shall be +3 mm, -0 of the nominal sheet size.

4.4.3 Flatness deviation shall not exceed 6% as calculated from the formula:

$$\frac{H}{L} \times 100 = \% \text{ Flatness Deviation}$$

where H = Maximum vertical distance between a flat reference surface and the surface of the sheet.

L = Minimum horizontal distance between the point where H is determined and the point where the sheet touches the flat reference surface.

A value of H less than 1.5 mm shall not be cause for rejection. The maximum value of H shall not exceed 50 mm, independent of the value of L, as measured with the sheet resting concave side down on a flat reference surface.

5. Test Methods

5.1 Room Temperature Tensile Testing: A representative specimen from each sheet lot shall be prepared and tested in conformity with Tension Testing of Metallic Materials, ASTM E8. The specimen tested shall have a 25.4 mm gauge length and a 6.4 mm gauge width. Tensile properties shall be determined using a controlled strain rate of $0.005 \pm 0.002 \text{ min}^{-1}$ through 0.6% offset, then $0.05 \pm 0.02 \text{ min}^{-1}$ to failure. Specimens shall be taken transverse to the final rolling direction. Tensile tests shall be conducted at a temperature between 290 and 305 K.

5.2 Elevated Temperature Tensile Testing: Representative specimens from each sheet lot shall be prepared and tested in conformity with ASTM E21. The specimens tested shall have a 25.4 mm gauge length and 6.4 mm gauge width. Tensile properties shall be determined using a controlled cross-head speed of $1.3 \pm 0.5 \text{ mm/min}$ to failure. Specimens shall be taken transverse to the direction of final rolling.

5.3 Stress Rupture Testing: Representative specimens from each sheet lot shall be prepared and tested in conformity with ASTM E139. The specimens tested shall have a 25.4 mm gauge length and 6.4 mm gauge width. Temperature shall be continuously recorded by means of one thermocouple attached to the gauge section of the specimen. Specimens shall be taken transverse to the direction of final rolling. After twenty (20) h, stress may be increased in increments of 6.9 MN/m^2 per hour to failure in order to determine elongation.

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